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OF THE

AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS

(INCORPORATED)

Vol. 116

IRON AND STEEL DIVISION 1935

PAPERS AND DISCUSSIONS PRESENTED BEFORE THE DIVISION AT THE MEETINGS
HELD AT NEW YORK, OCT. 1-4, 1934, AND FEB. 18-21, 1935.

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Notice

This volume is the eighth of a series containing papers and discussions presented before the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers since its organization in 1928; one volume each year, as follows:

1928, Iron and Steel Technology in 1928
1929, 1930, 1931, 1932, 1933, 1934 and 1935, TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Iron and Steel Division

This volume contains papers and discussions presented at the meetings at New York, Oct. 1-4, 1934 and Feb 18-21, 1935.

Papers on iron and steel subjects published by the Institute prior to 1928 are to be found in many volumes of the TRANSACTIONS of the Institute; during the past 25 years in Vols. 37 to 45, inclusive; 47, 50 and 51, 53, 56, 58, 62, 67 to 71, inclusive; 73 and 75. Vol. 67 was devoted exclusively to iron and steel.

Iron and steel papers published in the TRANSACTIONS may be found by consulting the general indexes to Vols. 1 to 35 (1871-1904), Vols. 36 to 55 (1905-1916), and Vols. 56 to 72 (1917-1925), and the indexes in succeeding volumes.

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FOREWORD

In presenting this volume to the membership, it is our aim to live up to the high standards and traditions set by our predecessors in the Iron and Steel Committee and more recently in the Iron and Steel Division of the Institute. The papers in this volume constitute the majority of those presented at our annual meeting in February, 1935, and our fall meeting at the National Metals Congress in 1934. They represent a careful selection approved by competent readers and a painstaking and capable publication committee. Blast furnace, open hearth, mill practice, physical chemistry, physical metallurgy and applications are each the subject of papers showing the latest progress in the art. The high caliber of these papers leads to emphasis of the thought that the Iron and Steel Division is the only body of purely professional metallurgists in this country, and as such it behooves us to maintain both the technical and ethical standards of our activities and of our publication, avoiding commercial compromise and emphasizing those developments that are gradually but surely changing metallurgy from an art to a science.

The Howe Memorial Lecture was delivered by Earl C. Smith; his subject, "Some Problems of Steel Melting." Mr. Smith used a rather unusual and very effective method of presentation. In order to illustrate slag constitution, a petrographic microscope in conjunction with a projector threw the image of the sample proper on a screen visible to the audience and the appearance under either ordinary or polarized light with rotating prisms was strikingly demonstrated. Reproductions of some of the views are shown with the lecture in this volume. Francis M. Rich, whose paper "Some Observations and Theory on Slack-wind Blast-furnace Operation," was presented before the Division during the annual meeting last February, was the winner of the J. E. Johnson, Jr., Award for 1935. Neither the Robert W. Hunt medal nor prize was awarded in 1935.

Attention should be called to the excellent work being carried out by the Open Hearth Committee and the separate publication of the minutes of their Conference. The Open Hearth Conference, which is sponsored by our Division, represents a most successful open forum for interchange of information and mutual benefit to the participants. In the past year, the Conference on Physical Chemistry of Steelmaking

has been established, and it is expected that this will perform the same function as the Open Hearth Conference for those who are interested in the more scientific phases of the work.

The committees of the Iron and Steel Division have performed their function admirably, whether this function be reviewing prospective papers, organizing meetings or the study of specific problems. It is fitting on this occasion to express appreciation and give thanks to the many earnest workers who, without thought of personal gain, have contributed to the success of the Iron and Steel Division in the past year.

A. B. KINZEL, *Chairman*,
Iron and Steel Division.

NEW YORK, N. Y.
August 26, 1935.

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The Howe Memorial Lecture

THE Howe Memorial Lecture was authorized in April, 1923, in memory of Henry Marion Howe, as an annual address to be delivered by invitation under the auspices of the Institute by an individual of recognized and outstanding attainment in the science and practice of iron and steel metallurgy or metallography, chosen by the Board of Directors upon recommendation of the Iron and Steel Division.

So far, only American metallurgists have been invited to deliver the Howe lecture. It is believed that this lecture would gain in importance and significance were it possible to include metallurgists from other countries, but the Institute has not yet been able to do this on account of lack of special funds to support this lectureship.

The titles of the lectures and the lecturers are as follows:

- 1924 What is Steel? By Albert Sauveur.
- 1925 Austenite and Austenitic Steels. By John A. Mathews.
- 1926 Twenty-five Years of Metallography. By William Campbell.
- 1927 Alloy Steels. By Bradley Stoughton.
- 1928 Significance of the Simple Steel Analysis. By Henry D. Hibbard.
- 1929 Studies of Hadfield's Manganese Steel with the High-power Microscope.
By John Howe Hall.
- 1930 The Future of the American Iron and Steel Industry. By Zay Jeffries.
- 1931 On the Art of Metallography. By Francis F. Lucas.
- 1932 On the Rates of Reactions in Solid Steel. By Edgar C. Bain.
- 1933 Steelmaking Processes. By George B. Waterhouse.
- 1934 The Corrosion Problem with Respect to Iron and Steel. By Frank. N. Speller.
- 1935 Problems of Steel Melting. By Earl C. Smith.



EARL C. SMITH

Henry Marion Howe Memorial Lecturer, 1935

Some Problems of Steel Melting

BY EARL C. SMITH,* MEMBER A.I.M.E.

(Henry Marion Howe Memorial Lecture†)

AT this meeting, one of a series, we are gathered to share with each other the experiences of our times. The American Institute of Mining and Metallurgical Engineers and similar organizations are largely possible because of the attitude of mind of our teachers. To their cult, we, industrial technical men, owe our place in the affairs of our time. To our teachers we owe an obligation which we should repay by training the generation that is to follow.

Education is a process of drawing out. The educator may occupy a modest station in life's affairs, or a position of honor. If, however, he adds to the stores of human usefulness by training, mentally or manually, those with whom he associates, he belongs to that great, usually unselfish, group known as teachers; those who through the ages have gathered the important things known to man, classified them for useful purposes and imparted them to others that man may live more usefully.

To my teachers, who, through the years, have added to my store of knowledge, I wish to acknowledge publicly my obligation for the intimate contact with the subject matter of this discussion.

It was my privilege to become acquainted intimately with a microscope under the guidance of Dr. W. J. McCaughey, at Ohio State University, in the study of microscopic mineralogy. To study opaque material led me to Prof. D. J. Demorest, at Ohio State University, whose interest in my education sent me East for more special work in metallography.

At Columbia University I came directly under the guidance of Dr. William Campbell. At that time, still active, guiding from the background, was the man to whose memory we do honor today. To him, many of us present owe an obligation, for who can say what part of our training originated in the mind and activity of this teacher, our teacher, Dr. Henry Marion Howe.

The background of an education is apt to be extremely varied. No measure has ever existed to determine what the human mind can comprehend. We, therefore, have no possible chance to predict to what use the industrially inclined human mind may turn the information that comes

* Chief Metallurgist, Republic Steel Corporation, Youngstown, Ohio.

† Presented at the New York Meeting, February, 1935. Twelfth Annual Lecture. Manuscript received at the office of the Institute Feb. 21, 1935.

within its grasp. Helmholtz, in a speech on Goethe, said: "He who knows the laws of the phenomena, thereby not only obtains knowledge, but also the power of interfering with nature in the proper moment, and of having it work according to his will and his advantage."

Our problem is to acquire knowledge of the laws of the phenomena of melting this very practical material called steel; this alloy, essentially iron and carbon, which in our generation is cast in an initially malleable mass. If we can obtain the power to interfere intelligently with nature, we may let it work to our advantage, even in a monetary way.

THE ART OF MAKING AND MELTING STEEL

The art of steel melting is very old and steelmaking is older than steel melting. The steel of history has all but disappeared from commercial production. This steel of history, best known to our generation as carburized wrought iron, called blister or shear steel, was replaced, first, by the crucible cast steels, and later, by the big tonnage methods. Any method of steelmaking that produced pasty material offered slight opportunity for control. The most satisfactory insurance was to average the errors by working the product together a number of times until the whole was as uniform as possible.

With the advent of crucible melting, in nations with more technical minds, it soon became evident that it was possible to vary the product during manufacture. The early stages of our present attempts to "interfere with nature in the proper moment" were the experiments of the crucible melters. The results were so useful that crucible melting became important and paved the way for the subsequent inventions that led to the methods known as the bessemer process, the open hearth, and the electric furnace.

Of these methods the, so-called, basic open hearth dominates the industry of the world; the bessemer process is second; the other methods are important, but not large tonnage producers. If in this presentation it seems that the basic open hearth is overwhelming in its dominance, it must be considered that in our nation the basic open hearth produces more than four-fifths of all the steel we consume. It can make steel from such variable raw materials, and under such a wide variety of conditions, that it represents a splendid example of an industrial idea that has but started on its way. It presents many problems. Some will be outlined in the contained subject matter with the hope that more exact knowledge may be obtained from specialized study by those equipped to handle the different phases.

To melt steel requires a structure capable of withstanding temperatures close to 3000° F. The furnace structure must be within economic bounds, established by the commodity under consideration. Thus, the electric-furnace steels may be produced on bottoms of higher cost than

those used for the simpler open-hearth steels. The furnace structure is an assemblage of varied materials, each selected by experience, to construct a workable tool.

GENERATION OF HEAT

The generation of temperatures close to 3000° F. has been mastered commercially in many ways. We have electrically heated units capable of commercial temperature far in excess of this figure. The method of generation of heat and the upper commercial limit are of extreme importance. We are concerned with a series of reactions that never reach equilibrium. In fact, they approach equilibrium from but one side. Commercially, we never reverse and make the pig iron in the steel-melting unit. It is important that we know the time element and the temperature element, for what we can accomplish with increased time can usually be hastened by increased temperature. We are, therefore, concerned with the heat-generating scheme as a variable in a complicated shifting set of conditions. We are not working with known phases in a closed system.

Commercially, we have two major heat-generating schemes. We burn fuel, which, in principle, means a combination of gaseous material with air. In practice, such a condition is oxidizing, and has a commercial peak but little in excess of the required 3000° F. We may generate heat by electric current, in which case we can commercially exceed the required 3000° F. by a rather substantial margin. We can further keep the gaseous phase of the system more reducing. We have here a fundamental variable to use. Our problem becomes one of selection of the open-hearth furnace as against the electric furnace. The proper choice must depend upon the reactions required: the open-hearth furnace, where oxidizing reactions are desirable, and the electric furnace, where reducing reactions are more useful.

REFRACTORIES

Above the melting hearth the material selected to withstand the temperature is silica brick. If its peculiarities are properly understood, it is an extremely able material. Commercially, it is silica bonded with lime and burned at a temperature, and for a time, sufficient to convert more than half the quartz to the form of cristobalite. In service, a further change takes place and in the high-temperature service, when properly handled, the working surfaces are the modification known as tridymite. Silica is peculiar in that the modifications have successively higher melting points; the melting point of tridymite is 3339° F.; the melting point of cristobalite is 3414° F. Neglecting the volume changes, which are important, mainly below working temperatures, we have a refractory that will stand more abuse in heat if we provide time for phase changes.

The commercial range of usefulness is extended nearly 200° F. by proper handling, to approximately 3015° F.

The contamination of the exposed surfaces of the silica brick brings about an interesting set of conditions. The condition of service most desirable is a fair degree of oxidation. The metallic splash is converted to iron oxide and, strangely, hardly combines with the silica as long as it is kept oxidized to the higher form of oxide. The basic slag materials with which the silica comes in contact combine rather readily, but the iron-silica combination is very intimately associated with the degree of reducing conditions. The section of a roof brick after a service campaign shows, in the working face, a large amount of crystalline tridymite twins, a small amount of magnetic oxide of iron, and a still smaller amount of ferrous silicate. If the amount of iron oxide present were all combined as ferrous silicate, the mass would soften quickly. If the conditions in a furnace were to become definitely reducing for even very short periods of time, the magnetic form of iron oxide would be reduced, with the resulting formation of the lower melting iron silicate. Destruction of the silica refractory would result. As much as an inch has been destroyed on a basic open-hearth furnace roof in less than five minutes, in experimental work involving reducing atmospheres. We have, therefore, a problem of control of oxidation at the roof-gas interface at times when it may be highly desirable to have strictly reducing conditions at the gas-slag interface.

In the smelting zone of the primitive furnaces, the construction was very similar to the clay crucible of history. This admirable melting unit was essentially a silicate and was attacked by the molten metal with such ease that the steel produced carried fairly high silicon. It was, we may say, an easy step to the sand bottom in the hearth-type furnaces and the vessels used in the bessemer method. The acid melting hearths reacted directly with the bath and were depended upon to produce, in part, the desired chemical analysis. Within certain limits of chemistry it is possible to establish, commercially, equilibrium between the molten metal, the bottom, and the slag at given temperatures, in the acid open hearth. High-quality steels are made, under proper conditions, by these methods. Economically, the acid methods have been forced into fields of high-cost limited usage.

With economic conditions again favoring the bessemer practice, this process will be found much more widely useful. The reactions involved correspond very closely to the acid open hearth. The time element of the reaction is so short that it seems impossible to obtain equilibrium. A section of a slag from the vessel shows the partially combined siliceous material eroded from the lining.

Since the basic open hearth dominates the steel-melting production, the more general hearth material is that group of refractories known as

basic refractories. These are essentially magnesia materials. An important factor in the satisfactory service they render is the relation of magnesia and dicalcium silicate (2CaOSiO_2), the usual bonding material, to the slags and metal encountered in the steel-melting process. Dicalcium silicate furnishes an infusible bond which is also but sparingly soluble in the slag with which it is brought into contact. These materials make up the basic open-hearth bottoms on which, in our age, are melted the steels of the world.

The simplest basic bottom is made directly from raw dolomite and burned in place in the furnace. The nearly pure carbonates, when burned, are subject to considerable shrinkage, burning to a porous mass which is so refractory that it requires fluxing before it bonds into place for proper service. They have so many obvious weak points that they may be considered as impractical for bottom construction.

A useful modification of this practice is the facing of the working area of the more stable bottoms with a layer of raw dolomite. This practice is common in the smaller plants which do not have sufficient consumption of refractories to justify a calcining plant.

The next logical step is to calcine, or clinker, the dolomite outside the furnace and use this prepared material as a facing. This practice is commonly used. The working layer is quite high in lime and these bottoms can be seen to have large amounts of dicalcium silicate present when the bottom is in active use.

The commercial practice most favored in our country, in building a melting hearth for basic steelmaking, is to bond magnesium oxide with some material, keeping it as pure as the operation will tolerate, and on this to carry a working face as refractory as the operation will permit. This means we vary the quality of the refractory with our ability to work it into our structures. Pure, or nearly pure, magnesium oxide, in the form of electrically sintered periclase, is used in electric-furnace bottoms. The bond in electric furnaces may be water glass, sufficient to make the particles adhere when cold. The mixture is rammed into place and a monolithic bottom results. The working face is prepared from materials that bond at more reasonable temperatures. Less refractory magnesium oxide products are used in open-hearth work.

This choice of magnesia is largely influenced by two important properties of this material; it is pyroplastic; and is the only material, commercially available, that will absorb more than half its weight of iron as FeO before the fusibility is lowered to a dangerous point. We may expect that our permanent base in service is soft but not liquid, resisting thermal shocks and erosion in a remarkable way. Since it does not react commercially with the molten metal, we need not anticipate a chemical change of the metal during melting.

The drawback is that pure magnesium oxide is too refractory for use alone, and accessory fluxing materials are difficult to incorporate uni-

formly. Nature has provided for us, in Austrian magnesite, a less pure form which is very useful in the lower temperature ranges encountered in the basic open hearths. The calcined product of this Austrian magnesite produces molecularly dispersed iron oxide, and is a material that can be bonded solidly at usual working temperatures.

The procedure in making a new bottom is to mix with the calcined magnesite an amount of open-hearth slag. This slag, which carries lime and silica with ferrous iron, combines with the outer layers of the calcined magnesite. The cubical particles of calcined magnesite are made somewhat spherical in the operation, owing to the solubility of the corners, and the resulting sections show cubical cleavage lines, crossing essentially circular plates, due to sectioning. The iron oxide, dissolving slowly into the calcined magnesite grain, gives an edge stain that increases if the surrounding medium supplies the required iron oxide. Continued supply of iron oxide results in the lowering of fusibility; the outer layers of the grain melt and join the slag. The failure is as slow as the surrounding conditions dictate. Thus we may expect no erosion when the iron oxide or other fluxing material is limited. We must anticipate, in making low metalloïd content materials, such as open-hearth irons, that the bottom fluxing will be increased. The penetration rate is slow, therefore only the outer layers are damaged. Even after extensive damage due to making highly oxidized steels, it is quite safe to reface with calcined magnesite, burn to establish a bond, and proceed with the melting operation. Where the carbon content of the steel does not fall below about 0.30 carbon in the furnace, the damage to the bottom by oxidation products is not enough to be a factor. In such melting practice the reverse is true; the slags are so refractory that they become incorporated into the bottom.

It is of interest to show a section of a bottom in which manganese oxide, as a bottom material, replaced magnesium oxide, by the process of building up from slag. There are the same cubical cleavage lines showing across circular areas, the interstitial mass being a silicate very similar in character to the corresponding calcium silicates which bond the basic open-hearth bottom. If manganese were sufficiently cheap, it might serve as a bottom material for certain high-manganese steels, but such a bottom would react freely with the molten metal. This specimen was furnished from the collection of Prof. W. J. McCaughey, Ohio State University, and represents a section of the slag that formed this experimental furnace bottom.

It is highly desirable to have, for our furnace bottoms, an economical material that will remain inert under the widely varying conditions encountered in service. If such a bottom material were available, we could eliminate one variable from the now too complicated system of gas, slag, metal and hearth. There is no indication of this ideal hearth at this time.

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the relation to this system CaO-FeO-SiO_2 to the quaternary system when manganese oxide is present, we will be far toward solution of our commercial problem.

The physical appearance of the slag has been used for some years, both here and abroad, to guide the melter in handling the furnace. Good

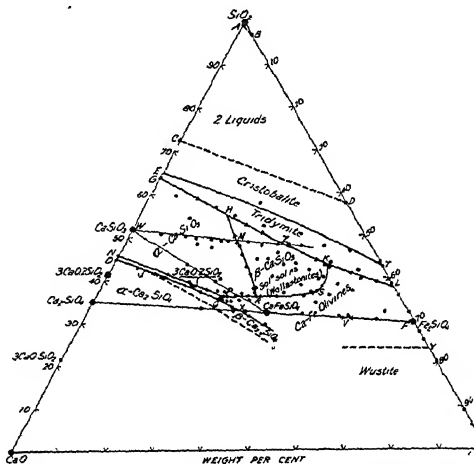


FIG. 2.—EQUILIBRIUM DIAGRAM OF PART OF SYSTEM CaO-FeO-SiO_2 , SHOWING FIELDS OF STABILITY OF CRYSTALLINE PHASES IN CONTACT WITH LIQUID (Bowen, Schairer and Posnjak).

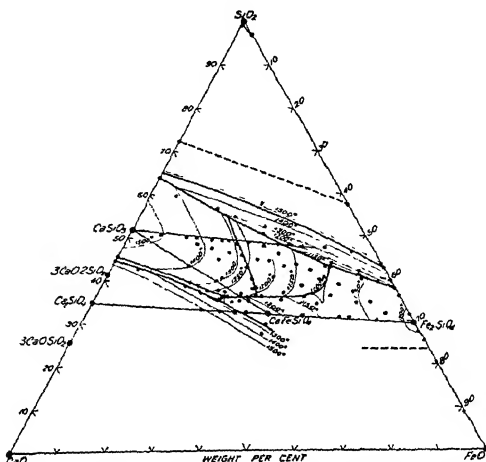


FIG. 3.—SAME AS FIG. 2 WITH ISOTHERMS ADDED (Bowen, Schairer and Posnjak).

descriptions of the appearance have been presented by several writers. The study by Janitsky² shows very clearly much pertinent information.

The study, recently, by Back³ is quite comprehensive. This very useful addition to control methods is hardly more complicated than the blast-furnace slag test, which is very old. Continued observation will

² Janitsky: American Iron & Steel Inst. (1929) 417.

³ Back: *Stahl und Eisen* (Sept. 13, 1934) 54, No. 37, 945-954.

establish this as an additional method of control in a practical way. The melter foreman will then consider it equally as important as his metal test. The glassy slags of the acid open-hearth steels are observed and furnish very important information.

To develop more information concerning the factors involved, some hundreds of slag tests, sampled much after the methods described by earlier authors, were sectioned for study. Additional studies, using reflected light, are under way. This method is simpler in specimen preparation, but does not offer the extreme contrasts in color, so useful in identification of the phases visible in thin section. Due to the very large areas easily prepared, this will probably be the useful method in the longer time studies.

The study of slag samples proves that we are not working with a homogeneous liquid phase. One can see, and actually feel with a bar, lumps of undissolved and uncombined material in the liquid slag. Any method of sampling will produce distinct evidence of incomplete equilibrium in the way of partially combined products. We are dealing with a subject that can be approached best on the basis of personal observation of facts, the explanation of which lies in the future.

We encounter some very characteristic slag structures in our study. We encounter similar structures from such widely varying operations that it is reasonable to assume that these structures are associated with some very definite conditions. The association of these structures with practice is either not known or, at least, not widely published.

Acid open-hearth slags are essentially the product of oxidation of the metal itself. The melt-down slags, in basic open-hearth melting, have many characteristics of the acid slags. These early basic slags are nearly colorless in section and have, usually, a greenish cast on the splintered edges. They are, however, much higher in basic components and therefore are different, chemically, from the acid type. They have the ability to dissolve iron oxide and hold it in solution as a silicate of iron. In this form the iron oxide is inert as an oxidizing medium, and the slags are very inactive.

PETROGRAPHIC STUDY OF SLAGS

These basic melt-down slags, when examined in thin section under the petrographic microscope, are seen to be composed almost entirely of a single crystal phase, a transparent silicate, with little or no free oxide present. As the heat progresses, these slags change their character with a striking difference in appearance.

The thin section of this new type of slag is dark colored and is seen as a multiple-phase system. The transparent particles, seen as white areas when contrasted with the dark oxide areas, have the essential composition of dicalcium silicate. Its persistent occurrence in slags, as sizable grains,

indicates limited ability to pass into solution in the liquid portion of the slag. Its rounded form, with fairly regular outline, indicates only a slight solution effect. The dark phase of the system is difficultly resolvable on account of its almost black color, but it has been, probably, the fusible part of the system because it occupies the interstitial spaces. It is essentially oxide of iron and manganese but, on account of low translucency, petrographic identification was replaced by X-ray analysis.

As we sample the early slags, we find lumps floating in the liquid. These may be so large that they weigh several pounds. They are covered with a characteristic shell which is thin, compact, and impervious, almost a glaze over the lump. In the thin section this glaze is almost white, with a blocky appearance. This shell is dicalcium silicate (2CaOSiO_2), carrying with it an unknown amount of dissolved materials. As we progress to the center of the lump, we note that the white gives way to a honey yellow material, which seems to fill the interstitial space of the dicalcium silicate (2CaOSiO_2). As we progress further, we notice that the yellow darkens to a brown; the center may be nearly clear lime. The structure at higher magnification appears to be a series of veins of yellow into the white grains, which are edged with brown. In rare cases, in basic open-hearth work, the brown is associated with a deep red material.

The floater lump of lime is in the process of decomposition and a probable explanation of this decomposition is of interest. The slag in the early stage is essentially the oxidation product of the metal itself, yielding a large amount of fusible silicates which bathe the colder, partially or completely burnt lime. Reaction takes place at the low temperatures of the early stages. The lime, which has a high affinity for silica, reacts with the molten silicates and forms a coating of dicalcium silicate (2CaOSiO_2) on the lime lumps. This coating is extremely infusible. Dicalcium silicate has a limited solubility for the other metallic oxides. The result is the formation of fingers of dicalcium silicate (2CaOSiO_2), surrounded by an oxide phase in which are combined iron oxide, manganese oxide, and lime. As long as silica is available for this reaction, it can proceed with the commercial result of an increasingly infusible slag. When the silicate of this mixture is converted into dicalcium silicate, there remains an excess of metallic oxides and lime to form calcium ferrites, which are low-melting-point materials and are not particularly stable.

It is of interest to follow the changes of a slag from the melt down to the very extreme stage encountered when making the very low-carbon, low-manganese material. The series is best portrayed by selecting type slag sections rather than those from a single heat of steel. The difference in the slag produced in the practice of making one type of steel, from those of other types, or analyses, is definite but not marked. By selection of type sections from several heats, a sort of standard set has been collected.

In the early basic slags of the heat an acicular structure is the most commonly encountered appearance. Usually two phases are present. In rare cases, the black-green phase is present in but limited amounts and the slag may be nearly colorless in thin section. In the normal operation of the furnace, an increasing amount of fluxing material, in the form of lime, is brought into the slag. The reaction with the lime is slow and is marked by the disappearance of the acicular structure. The slag is now formed of particles of dicalcium silicate (2CaOSiO_2), the disintegrated coating of the lime lumps, surrounded by a black-brown mass which shows the lacy radial structure of the breakdown stage. Such a slag is not active enough to make time in soft steelmaking and represents the raw slag of the furnace operator's descriptive distinctions. Where the raw materials are low enough in sulfur and phosphorus, such a slag is about as far as is required in simple steelmaking. If, however, the plant requires a product that demands other than proper carbon content and a satisfactory pouring temperature, it becomes necessary to carry the operation further. If a low oxidized heat is required, the operator proceeds from this point cautiously. The heat is melted until clear and all the lime is up, so that a known basicity is present. If the slag is too sticky, the operation of thinning down may be by heat, fluor-spar, or additions of ore and burnt lime. If the heat is for a type of steel demanding high oxidation, or the slag is not basic enough, the operator proceeds to add lime after all the lime is up from the bottom.

The addition of lime causes the formation of calcium ferrites, which are active in promoting solution of dicalcium silicate. A definite change in color results; the yellow-brown gives way to a red-brown. The red-brown slags, when fully matured show, in thin section, a fine-grained, mosaiclike structure. The low-metalloid steel slags and open-hearth iron slags in thin section are black-red in color and fine grained. The change of color is explained by the fact that the yellow-brown slags are mixtures of nearly colorless dicalcium silicate (an oxide phase which is honey yellow), and brown dicalcium ferrite ($2\text{CaOFe}_2\text{O}_3$). The color impression of this mixture is a yellow-brown. As the amount of dicalcium ferrite increases, the nearly colorless dicalcium silicate no longer exists in the large primary grains. The distinct increase of red-brown coloring material causes the thin section to show this color. In the extremely basic slags, with high iron oxide content, red, needlelike crystals of monocalcium ferrite (CaOFe_2O_3) appear, giving the thin section a red-black appearance. The calcium-iron oxide compounds are described by Boike Eitel⁴ and Winchell⁵ and additional compounds are reported by Martin and Vogel⁶.

⁴ Boike Eitel: *Grundlagen Physik. Chem. Petrographie*, 11 Auflage.

⁵ Winchell: *Microscopic Character of Artificial Minerals*.

⁶ Martin and Vogel: *Arch. Eisenhüttenwesen* (December, 1934).

Killed steels of the low oxidation type are made under slags of the yellow-brown color, in section; rimming steels under slags starting to show red-brown, in section; and also entirely red-brown. Low-metalloid steel slags and open-hearth iron slags are distinctly red-black in thin section.

Occasionally an excess of lime is present, due to low silica in the system, and the lime is sufficient to permit the formation of tricalcium silicate (3CaOSiO_2). In such slags the tricalcium silicate is present in lath-shaped particles resulting from the sectioning of the tabular crystals in which it occurs, and it is usually associated with long red needles of calcium ferrite. Probably the red-black color of the low-metalloid steel slags and open-hearth iron slag is due to this same deep red phase in finely divided condition.

IDENTIFICATION OF MINERALS

At this stage it is well to discuss the lack of positive identification of the minerals encountered. Practically none of the slag constituents occur as natural minerals. Two reasons might be offered for this peculiar condition. Rocks of basic igneous materials are uncommon. In the whole of North America, it is estimated by Daly⁷, basic rocks comprise less than 0.1 per cent of the igneous rocks known. When to this fact we add the complication of sudden formation, such as is encountered in steel-melting practice, we have many reasons to believe that natural minerals, corresponding to these slags, will hardly be found. Confirming this is the fact that beta dicalcium silicate (2CaOSiO_2) occurs as larnite in one spot in the world—at Larne, Ireland.

Beta dicalcium silicate, a common mineral constituent of basic open-hearth slags, is also present in certain basic electric-furnace slags, particularly melting or oxidizing slags. The finishing slags of basic electric-furnace melting have this mineral present, while partially cooled, but at approximately 1250°F. an inversion takes place, changing to the gamma form, with a volume change which shatters the mineral. For this reason slags in thin section of basic electric-steel melting are uncommon. Dissolved materials present in the dicalcium silicate in the open-hearth slags prevent this inversion.

As the practical application of the study of these slags progresses, more accurate information can be obtained regarding the composition and the properties of the constituent minerals. It represents a major problem of melting control, and will best be cleared up by the mineralogists of our universities and the Geophysical Laboratory of the Carnegie Institution working with carefully prepared artificial mineral specimens.

⁷ Daly: *Igneous Rocks and the Depths of the Earth*.

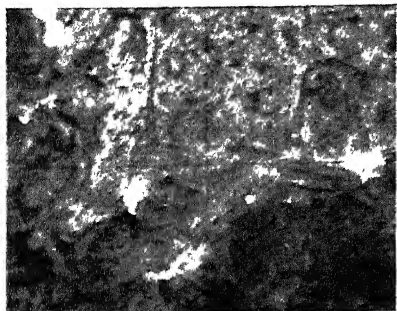
SOME PROBLEMS OF STEEL MELTING



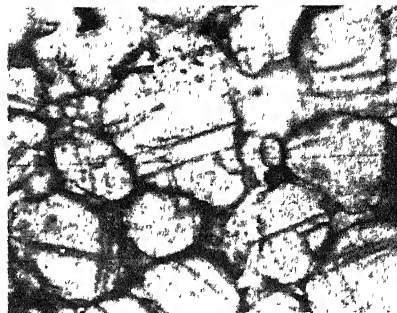
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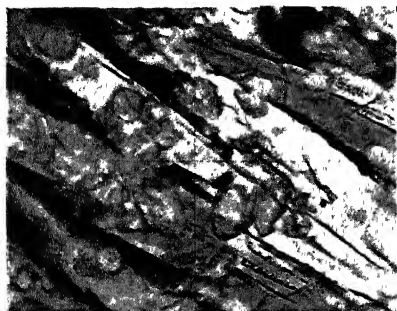
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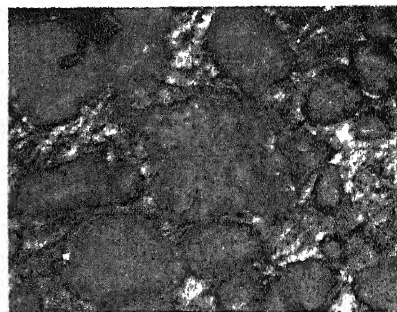
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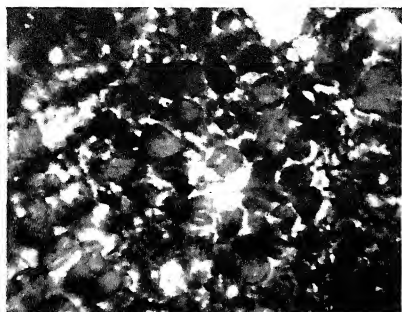
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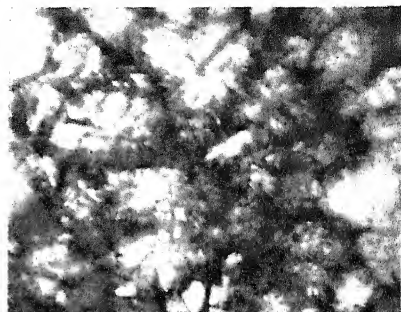
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1. Silica Brick Basic open hearth roof. Tridymite Twins developed in service. X Nicols
 2. Vessel Slag Acid Bessemer with some partially combined vessel lining.
 3. Working Face Basic open hearth bottom. Saturated Solid solution iron oxide in periclase, bonded by Dicalcium Silicate.
 4. Magnesite open hearth bottom. Deep below the working face.
 5. Early Melt Down Slag Basic open hearth Glaucocroite type, X Nicols.
 6. Manganese Oxide Slag from furnace bottom Bureau of Mines Experiment Station, Minneapolis, Minn.

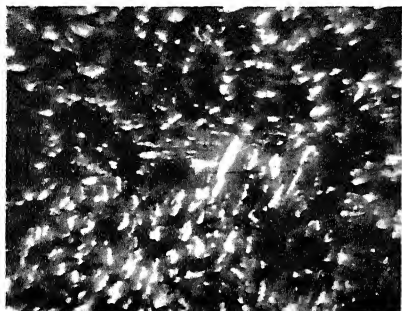
MAGNIFICATION 150 DIAMETERS ALL SECTIONS



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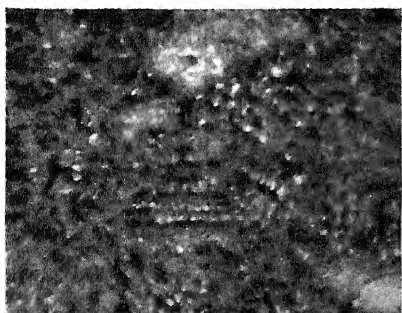
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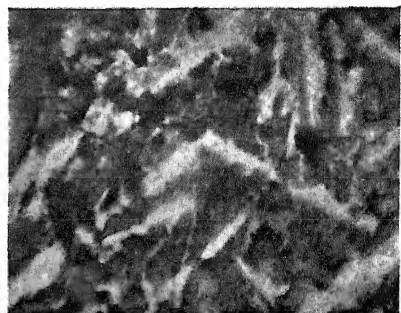
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7. "Raw" Slag Basic open hearth Primary Dicalcium Silicate and Oxide Phase.
 8. Low Effective Oxide Slag Basic open hearth Primary Dicalcium Silicate Major Constituent.
 9. High Oxide Slag Basic open hearth, Dark Constituent, Calcium Ferrite.
 10. Normal Finishing Slag for Soft Steel.
 11. Very Basic Open Hearth Slag Mosaic Like Structure of Mature Slag of Low Carbon Steel.
 12. Very Basic Low Carbon Steel Slag white phase Tricalcium Silicate Red Phase Calciumferrite.

THE PROBLEM IN STEELMAKING

We are face to face with the following problem: the refractory hearth reacts with the slag in the basic furnaces, and with the slag and metal in the acid furnaces. So long as we work on a partially known bottom, we may expect critical problems in melting equilibrium. A pyroplastic material is needed for bottoms, which is inert to slag and the metals melted upon it.

The roof and wall materials of the furnaces are barely safe at the present operating temperatures. Both research and practical experience indicate that sulfur problems would be lessened if higher temperatures could be used. We could use construction material that is insensitive to heat shock and capable of operating at 3500° F.

The working conditions that we are studying are at temperatures close to 3000° F., and we know too little of the relation of the molten slag, which is a liquid with an intermixture of solids, to the solid slag, which we investigate by chemical or other means of analysis remote from its natural environment. Thermal, chemical and mineralogical studies will clear up much of the lack of information that troubles us. If we could, with certainty, sample the slags and know that our results paralleled the heat or the action within the furnace, we would be far along our way. Comparative results indicate that most of the methods of sampling are satisfactory for the microscopic study of the undissolved phases.

There are very definite problems involved in sampling for chemical analysis. Whether the trend in the future will be toward physical mineralogical studies, or quantitative and physical chemistry, depends upon which method is best served by the samples obtained.

We who are interested in the commercial aspects of melting control have before us the problem of providing facilities for the men who will work upon this and similar problems. We know that, in the generation preceding ours, the thinking minds of steel metallurgy were focused to a large degree upon the metallic portions of the system. This problem of the metal was, in their day, the more important aspect of the major problem. We know that in repeated cases men proceeded part way on slag-control studies only to find the problems of the metal itself so far from solution that no basis of control was intelligent. It would be well to remind ourselves that Dr. Howe was originally interested in the slags as well as the metallic products.

We should give aid to those who in our day are exploring fields that are accessory to the main work. From their efforts will come the important discoveries of our generation.

Some Observations and Theory on Slack-wind Blast-furnace Operation

BY FRANCIS M. RICH*

(New York Meeting, February, 1935)

BEFORE the world-wide depression, the primary purpose of most blast-furnace operators was to produce a maximum tonnage of pig iron per day for each furnace in blast. Some attention was paid to the conservation of labor and raw materials, but the idea was well established that low-cost pig iron was attainable only when each furnace was producing a high tonnage.

After the depression had set in, the picture changed considerably. Each blast-furnace operator was forced to run his plant in a manner that best fitted the economical set-up of his company. A great deal of thought was expended on the different methods of operation, always with the idea of making each product in a way that would best serve his company financially. Because of this abnormal condition, the blast-furnace man was compelled to indulge in various practices of which many had been believed to be next to impossible up to that time. The ultimate purpose of these innovations was either one or a combination of the following:

1. To produce only enough pig iron for immediate consumption at a minimum cost.
2. To produce gas for boiler or mill use to supplant some higher priced fuel.
3. To consume the coke produced at the coke plant, which was often viewed as a byproduct.
4. To protect the cash position of the company.

These conditions were met by diverse methods, some of which were:

1. Slow or decreased wind. In some instances the blast blown was held as low as 25 per cent of the normal volume.
2. Intermittent operation, in which the furnaces were shut down or "fanned" at frequent intervals.

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* Superintendent of Blast Furnaces, Republic Steel Corporation, Youngstown Ohio.

3. Slow wind for a week or so, then normal wind for a short period. Each substantial change of wind was often accompanied by a change of burden, to produce a different grade of iron.

It is needless to say that in spite of these methods the operators were required, more than ever before, to produce iron of excellent quality to meet the keen competition of other companies and the rigid specifications of customers. That the blast-furnace man has fulfilled these obligations is a tribute to his ingenuity, courage and skill.

FUNDAMENTAL REQUIREMENTS OF SUCCESSFUL SLOW-WIND OPERATION

Many volumes could be written on the experiences of the blast-furnace operators during the depression, but in our opinion the slow-wind operation has done more towards perfecting blast-furnace technique than any other development. Most furnacemen have found that lowering the wind on the furnaces meant a decrease in fuel consumption and flue-dust losses, in spite of the fact that there were many "sick" furnaces before the fundamentals of success for slow blowing were appreciated. An inspection of these fundamentals reveals nothing new to the blast-furnace man, but we are convinced that an infraction of these rules is accompanied by far more serious results on slow wind than on normal wind. These principles have been proved many times in practice and are tabulated below:

1. The furnace lining must be in fairly good shape. The brickwork should not be cut out or built up excessively and the walls of the furnace must be kept clean at all times. The lining should be plumb, the ideal condition being that the traces of all horizontal planes with the inwall shall be perfect circles, the loci of whose centers shall form a straight vertical line, which is the true center line of the furnace.

2. The top-charging mechanism must be correctly designed, located and operated. The vertical center lines of both bells and their respective hoppers should be co-linear with the true center line of the furnace in all positions. Both bells and their hoppers must be kept clean at all times. The distributor must be working correctly, and the entire charging equipment operating so that equal portions of each raw material are deposited in all sectors of the same size in the furnace.

3. The correct filling must be used. By this is meant that there are always a few methods of filling, with regard to the sequence and quantity of each raw material charged, that give the best results on the furnace under the operating conditions at the time.

4. Each raw material should be as nearly uniform in chemical analysis and physical properties as possible; also, each material should be weighed and measured correctly at all times according to the schedule determined by the operators.

5. Enough slag volume should be carried to run the furnace on a lean or glassy slag, if the raw materials and the sulfur-content limits of the product will permit. Some plants are limited in this matter because the slag is used for commercial purposes and must meet the tests of the customers successfully. It is the general opinion that more slag volume is required as the wind is decreased.

6. The blast distribution must be uniform in temperature and quantity at each tuyere, or at least at each pair of adjacent tuyeres.

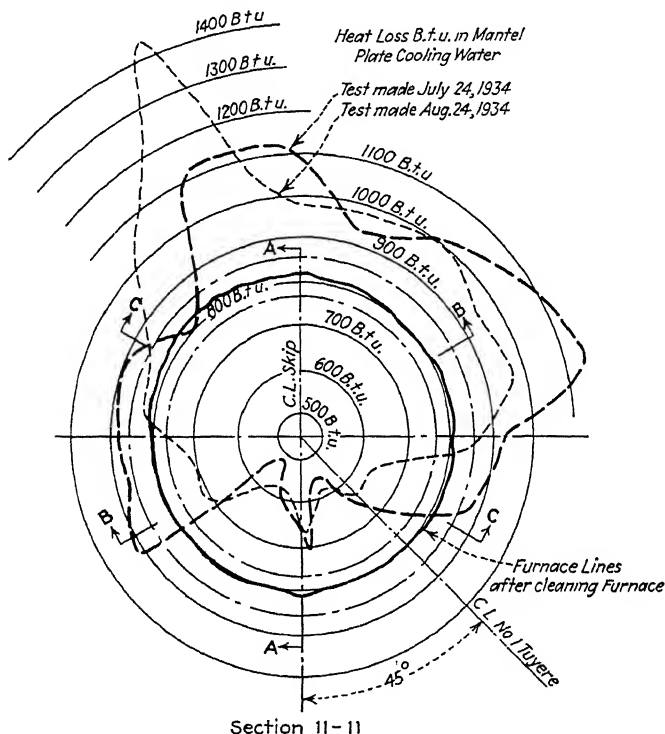


FIG. 1.—COMPARISON OF FURNACE LINES AND HEAT LOSS IN MANTLE COOLING PLATES.

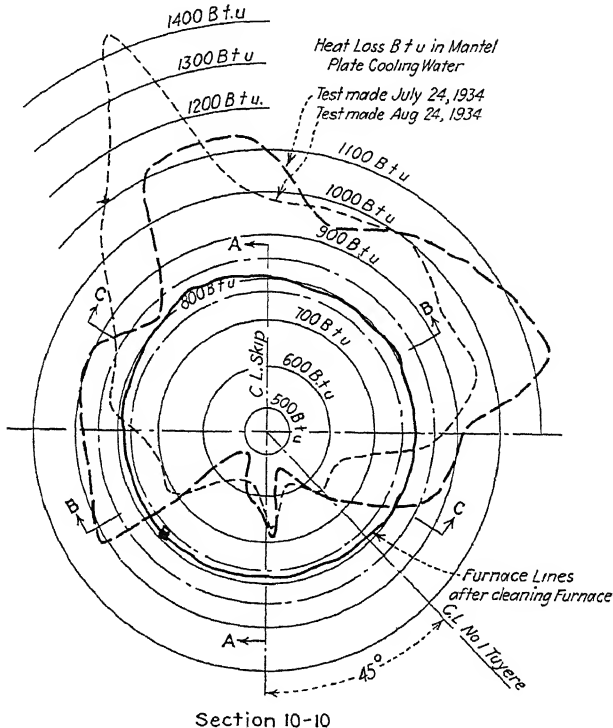
7. The correct size of tuyeres must be used to meet the operating conditions.

SOME EXPERIENCES IN CORRECTING FUNDAMENTALS

It is often difficult to keep a check on even a large part of the "commandments" mentioned above, but that is the best answer we can give to successful blast-furnace practice. A few of these problems with which we have been confronted have been very interesting from the blast-furnace man's viewpoint. Considerable research has been done recently, largely as the result of associated effort. Only experiences and tests that are of a pioneering nature will be dwelt on in this paper, inasmuch as

some of the methods for checking and correcting the rules mentioned are standard practice to the blast-furnace man.

We believe that the best way to keep an accurate check on a furnace lining is to install thermocouples in the lining, preferably at the beginning of the campaign. The hot junctions should be about 12 in. from the original inwall and the cold junctions connected to a multiple point recorder. This has proved very satisfactory in several plants. Another method is to determine the heat absorbed from the cooling water while



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FIG. 2.—COMPARISON OF FURNACE LINES AND HEAT LOSS IN MANTLE COOLING PLATES.

it is passing through the plates above the mantle. The plates should be blown out before testing, so that there will be no dirt left that would tend to insulate the copper. An example of this rather novel manner of testing is shown on Figs. 1, 2 and 3. Two tests were run exactly one month apart, and the furnace was blown out the day following the last test. These drawings show that the furnace was cut out slightly more on one side than on the other. The heat absorbed by the cooling water was much greater on the thin side.

If there is doubt in the operator's mind as to whether the furnace is cut out on the hot side or built up on the cold portion, test holes can be easily drilled to check the lining. If the lining is badly cut on one side,

the true center of the furnace is moved in that direction. The practice on the furnace will be improved if the charging apparatus is moved so that its center coincides with the new center of the lining. A great deal of checking should be done to determine the cause of the excessive wear, because if it is allowed to continue a hot spot is apt to develop, which may necessitate blowing out the furnace and patching the lining.

If the lining is built up, which we believe is more likely to happen on very slow wind, the usual remedy is to upset the filling in an attempt to clean off the "scabs." One furnace in the Chicago district had been working very poorly for several months. The coke consumption and flue-dust losses were high, which caused the operator to believe that his furnace was badly "scabbed up." He had several test holes drilled

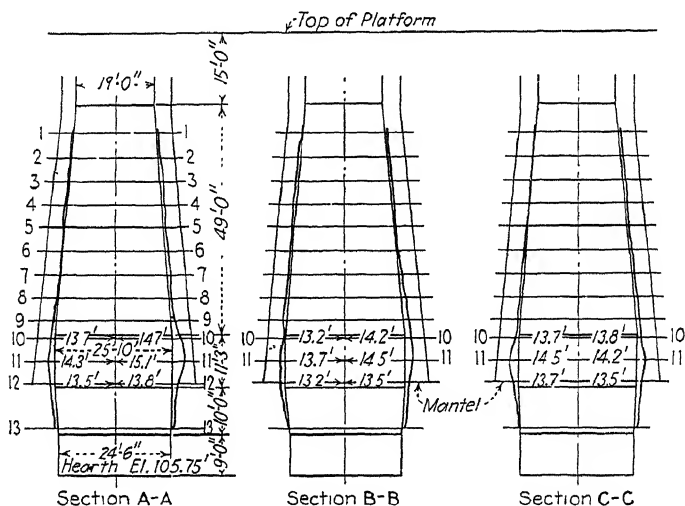


FIG. 3.—SECTION OF BLAST FURNACE A SHOWING FURNACE LINES AFTER CLEANING WALLS.

in the inwall and found this to be true. He also detected a strong odor of potassium cyanide at the holes. He immediately began to reverse the filling; that is charging coke to the bell first with the ore on top of it. This was done for several hours each day, the amount being increased on each succeeding day. In about four days the furnace "cleaned off," and made several high-sulfur casts of iron, after which she straightened out and ever since has been one of the outstanding furnaces in the country on slow wind.

The use of "cleaners" is a subject on which many furnacemen disagree. Some prefer to "slug" the furnace with charges of siliceous material, such as mill cinder, brick bats, bessemer slag or high-silica ore. We had one particularly successful experience with this type of cleaner. Furnace C, shown on Fig. 7, had not been working as she should. She was operating on 27,000 cu. ft. per min. of wind at the time, and was not

carrying the normal burden. The significant figures on this experience are given in Table 1.

TABLE 1.—*One Experience in Cleaning with Slugs of Siliceous Material*

| Day of Month | Theoretical Coke Rate, Lb. per G.T. Pig | Burden, Lb. per Charge | Average CO ₂ in Top Gas, Per Cent | Charging Slugs |
|--------------|---|------------------------|--|--|
| 19 | 1,957 | 20,000 | 12.7 | Charged 40,000 lb. of mill cinder |
| 20 | 1,892 | 20,600 | 12.6 | Charged 41,200 lb. of bessemer slag |
| 22 | 1,847 | 21,200 | 14.0 | Charged 20,000 lb. of siliceous ore every 8 hr. and continued. |
| 23 | 1,750 | 22,400 | 14.2 | |
| 25 | 1,702 | 23,000 | 14.3 | |

The first "slug" was charged on the nineteenth day of the month. About 14 hr. later the furnace was "sloppy" at the tuyeres and remained so for several days, although this condition gradually diminished. The furnace came up "hot," or high in silicon, as soon as the sloppy condition started, and burden was added at once to bring the silicon down. In six days, enough burden had been added to cut the theoretical coke rate down 255 lb. per gross ton of pig. This theoretical coke rate is very close to the actual coke rate, and is used because it is an excellent index of the furnace operation at the time. Because of this experience we prefer to "slug" the furnaces at regular intervals when the wind is brought down around 30,000 cu. ft. per minute.

The maintenance of a clean big bell is not nearly so difficult as it was before steeper angles of 50° and over came into use. There is still trouble at times due to baking of the material on the surface of the metal. One operator installed sprays in the gas seal, which kept the surface of the bell cool and thus prevented this baking of the ore. On slow wind most operators insist on keeping the bell empty until the furnace has reached a level where a charge can be put in at once, because of the comparatively long period of time between charges. Some operators charge so that the Mesabi ores, which usually are of a sandy nature, are first on the bell, and the more plastic Old Range ores, which often are high in alumina, are charged on top. Others use reverse filling or occasional charges of scrap to produce a scouring action on the bell surface. Constant inspection must be made in order to insure against this evil, as every furnaceman knows that a dirty bell means trouble.

The selection of the best filling is an age-old problem, which generally is solved by trial and error. Every furnaceman has his own methods,

which he has formulated from experience. The Bureau of Mines has done some excellent work in its investigations on this subject¹. It was the author's good fortune to become closely associated with Mr. S. P. Kinney² during his detailed investigations of three furnaces at the South Works of the Illinois Steel Co.; also to spend several afternoons with Mr. T. L. Joseph and other Bureau of Mines associates at the North Central Experiment Station in Minneapolis, and to obtain their views on the distribution of stock and gas in the iron blast furnace. These men have inspired us to perform some experiments on a smaller scale, in an attempt to correlate the conclusions reached by the Bureau of Mines men with the results obtained from actual practice. It is perhaps best to review the thermochemical reasoning so thoroughly covered by the Bureau of Mines *Tech. Paper* 476. We quote as follows from that paper³:

The work done in the upper shaft consists of (1) drying and preheating the charge, (2) first steps of reduction, (3) calcining the limestone. All of these reactions require a supply of heat. Therefore, the more uniform the contact between the gas and solid phases, the more effective will be the heat transfer and the sooner will the work be accomplished—within certain definite limits.

The advantage of doing as much work as possible in the upper part of the furnace is not apparent until the secondary reactions are considered. The secondary reaction that has the most bearing on the process is that of "Solution Loss," represented by the equation



This reaction does not occur at an appreciable rate below 850° C., but every time it does occur, it means that solid carbon has been lost to the process unless the resulting CO is reconverted to CO₂, either through reduction or carbon deposition (reverse of equation 1) further up the shaft. However, none of the solid carbon entering the gas stream through the medium of solution loss is ever completely recovered in the upper part of the furnace, so a distinct loss of efficiency is involved if any reaction producing CO₂ is allowed to occur at elevations in the furnace where the temperature exceeds 1,000° C.

The ideal condition is to complete the reduction of iron ore and calcining of limestone in the upper part of the shaft at temperatures below 1,000° C., allowing no production of CO₂ at temperatures higher than this. The more intimate the gas-solid contact in the upper part of the furnace, the more nearly will conditions approach

¹ S. P. Kinney, P. H. Royster and T. L. Joseph: Iron Blast Furnace Reactions. U.S. Bur. Mines *Tech. Paper* 391 (1927).

S. P. Kinney: The Blast Furnace Stock Column. U.S. Bur. Mines *Tech. Paper* 442 (1929); Composition of Materials from Various Elevations in an Iron Blast Furnace. U.S. Bur. Mines *Tech. Paper* 397 (1926); Effect of Sized Ore on Economy of Blast Furnace Operation as Based on Results of a 500-Ton Furnace. U.S. Bur. Mines *Tech. Paper* 459 (1930).

C. C. Furnas and T. L. Joseph: Stock Distribution and Gas-Solid Contact in the Blast Furnace. U.S. Bur. Mines *Tech. Paper* 476 (1930).

² S. P. Kinney: Reference of footnote 1.

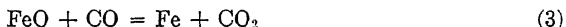
³ C. C. Furnas and T. L. Joseph: Reference of footnote 1, 3-4.

those in the ideal furnace advocated by Gruner⁴. Commercial operation never attains this ideal. Furnace investigations show that 20 to 80 per cent of the reduction is carried on below the top of the bosh, in the hotter part of the furnace.

So-called direct reduction—that is, reduction by hot carbon rather than CO gas—is another factor to be considered. It is debatable whether direct reduction occurs according to the equation,



or is a combination of the reactions,



and



The mechanism of the reaction, however, is a point only of academic interest, as the over-all effect is the same in both cases: that is, carbon is taken from the coke to produce CO, whereas the work could be done just as well with less carbon by producing CO₂ at lower temperatures. If reduction is completed at low temperatures, no iron ore is left to be reduced at high temperatures and consequently there are no secondary reactions that tend to diminish hearth temperatures. Hearth temperatures, necessary to complete desulphurization and reduction of silica, place definite limitations on fuel requirements. To maintain hearth temperatures, as much as the coke as possible should be burned at the tuyeres.

In other words, when some of the work of the upper shaft is performed by the heat of the hearth, which is available at high temperatures only, it is similar to heating a building with steam at 400-lb. pressure when steam at 2-lb. pressure would suffice.

It follows that in order that the upper portion of the stack may perform in the ideal manner, the gas-solid contact of the furnace must be perfect. This would mean that each particle of ore in any given horizontal plane must be in the same stage of reduction and that the gas analysis, temperature and velocity will be uniform at any point on this plane as a result. Such a condition does not exist in practice, although there are a few furnaces that have shown excellent test results with correspondingly good practice. The method of attack advocated by the Bureau of Mines⁵ was as follows:

1. Determine by experiment the gas-flow characteristics in the upper part of the furnace.

2. Correct the gas flow by means of changes in methods of charging.

At the time the experiments on furnace C were performed, we did not wish to go to the trouble and expense of drilling holes in the inwall,

⁴ M. L. Gruner: Blast Furnace Phenomena. Translation by L. D. B. Gordon, 28. Philadelphia, 1874. Henry Carey Baird Co.

J. E. Johnson, Jr.: Principles, Operation and Products of the Blast Furnace, 1, 75, 95. New York, 1918. McGraw-Hill Book Co.

J. W. Richards: Metallurgical Calculations, 274. New York, 1918. McGraw-Hill Book Co.

⁵ C. C. Furnas and T. L. Joseph: Reference of footnote 1, 38-39.

providing sampling tubes, etc., so it was decided to sample the gas at different points across the stock line by means of $\frac{3}{8}$ -in. pipes lowered through the try-rod holes and bent so that the points on the stock line and toward the center of the furnace could be reached. Generally two modified Orsat sampling machines were used simultaneously, each at a different try-rod hole. The CO_2 was usually the only determination

run, as the sum of the $\text{CO}_2 + \text{CO}$ in blast-furnace gas by volume is almost always in the range from 38 to 41 per cent. These try-rod holes were 9 in. from the stock-line wall, and after some experience samples were taken only at these 9-in. distances and compared with the average top-gas analysis to determine whether the gas was channeling up the walls or up the center. Many interesting results were obtained, some of which were of a very beneficial nature in regard to the practice on the furnace. In the period of a year 1017 CO_2 determinations were run, on samples taken at these 9-in. distances.

As a rule the conclusions of the Bureau of Mines paper on the results of filling with models⁶ were borne out. Fig. 4 shows the theoretical distribution of two different fillings at the stock line of this furnace, based on the theory propounded by the Bureau. The curves shown in Fig. 4c show the

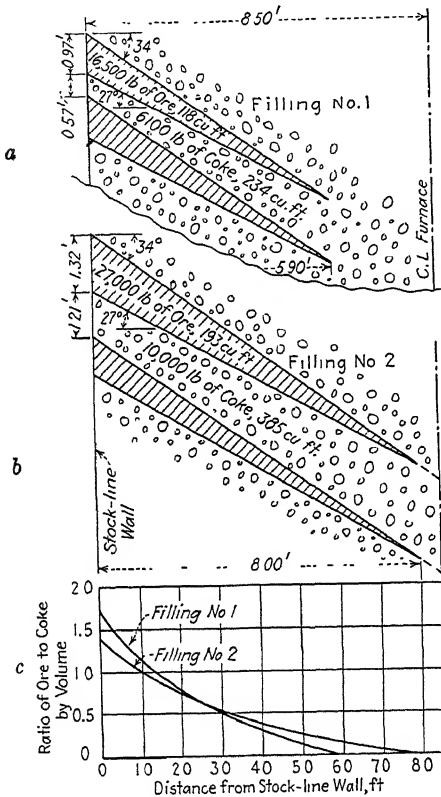


FIG. 4.—THEORETICAL FILLING AT STOCK LINE, FURNACE C.

volumetric ratios of ore to coke across the half section of the stock line. These curves show that the ratio of ore to coke is a maximum at the wall and decreases toward the center. Also, the filling with the heavier layer of ore has a larger ore:coke ratio at the center and a smaller ratio at the wall than the filling with the lighter ore layer. This distribution at the stock line is not the same as that at the midpoint of the upper part of the shaft, so we have given our ideas of the above-mentioned fillings, when they have reached this plane, in Fig. 5. This drawing shows a section of furnace C at a distance of

⁶ C. C. Furnas and L. T. Joseph: Reference of footnote 5

21.7 ft. below the normal stock level, visualizing the effect of the inwall batter. It is our opinion that this partly explains the more rapid movement of the stock at the inwall than at the center of the furnace, as proved experimentally by Kinney⁷.

We have seen actual evidence of this phenomenon. On several occasions, when the furnace was "blown down" to from 10 to 20 ft. below the normal stock line, the depth of the inverted cone of stock was much less than when the furnace was full. This indicates that the

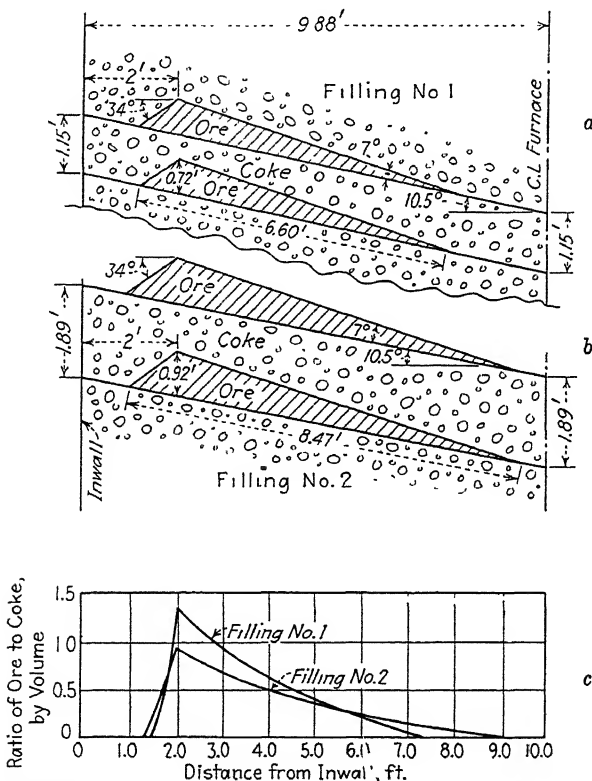


FIG. 5.—THEORETICAL FILLING AT MIDPOINT OF INDIRECT REDUCTION ZONE (21.7 FT. BELOW STOCK LINE), FURNACE C.

movement was faster at the inwall than at the center. The curves in Fig. 5c are somewhat similar to the average CO_2 curves for many furnaces. The ratios of ore to coke for the two fillings are somewhat similar to the data of Fig. 4. No account has been taken of the segregation of the fine and coarse material in the ore, although this plays an important part in blast-furnace distribution.

⁷ S. P. Kinney: The Blast-Furnace Stock Column. U.S. Bur. Mines *Tech. Paper* 442 (1929) 4, 19-24.

On one occasion the top gas was found to be very low in CO₂. The furnace had not been carrying the usual amount of burden, so immediately some tests were run on samples taken at 9 in. from the inwall. These showed the gas to be channeling through the center, so a heavier ore layer was charged, with gratifying results. Table 2 is a log of this experience. At another time it was found that the gas was traveling up the walls. A lighter ore layer was put on by a change in filling, after which the furnace straightened out. Table 3 gives a tabulation of the operations.

TABLE 2.—*Log of Tests When Gas Traveled up Center*

| Day of Month | Theoretical Coke Rate, Lb. per G.T. Pig | Top Temp., Deg. F. | Weight of Ore Layer, Lb. | Average CO ₂ , Per Cent | |
|--------------|---|--------------------|--------------------------|------------------------------------|----------|
| | | | | 9-in. Inwall | Ave. Top |
| 5 | 2,087 | 479 | 13,200 | | 10.4 |
| 6 | 2,183 | 488 | 13,200 | 16.5 | 10.4 |
| 7 | 2,083 | 471 | 15,000 | 16.5 | 10.8 |
| 8 | 1,977 | 441 | 16,000 | 14.2 | 13.7 |
| 9 | 1,839 | 362 | 17,100 | 15.8 | 16.3 |

The average wind blown at the time was 28,000 cu. ft. per min. at 60° F. and 30-in. Hg.

TABLE 3.—*Log of Tests When Gas Traveled up Walls*

| Day of Month | Theoretical Coke Rate, Lb. per G.T. Pig | Top Temp., Deg. F. | Weight of Ore Layer, Lb. | Average CO ₂ , Per Cent | |
|--------------|---|--------------------|--------------------------|------------------------------------|----------|
| | | | | 9-in. Inwall | Ave. Top |
| 1 | 2,110 | 410 | 16,800 | 9.0 | 12.0 |
| 2 | 2,068 | 410 | 14,400 | 13 0 | 15.5 |
| 3 | 1,907 | 380 | 15,800 | | |
| 7 | 1,730 | 310 | 17,500 | | |

The average wind blown was 42,000 cu. ft. per min. at 60° F. and 30-in. Hg.

It must not be concluded that the attempted solutions of furnace problems in this manner are always successful. Several times changes were made presumably in the right direction, with no beneficial effects on the furnace. We believe, however, that when the channeling of the gas is caused mainly by the use of a filling in which the size of the ore blanket is incorrect, the practice on the furnace will be improved by a method of procedure similar to that described above.

The uniformity of the blast-temperature distribution at the tuyeres is best checked by installing thermocouples in the tuyere stocks. Any discrepancy in these temperatures is due either to the incorrect location of the cold-air mixer-line connection with the hot-blast main or poor design or location of the hot-blast main itself. We ran tests of this

nature on three furnaces operating in the same plant with hot-blast mains of the same size and design, but with different mixer connections. The mixer connections were located: (1) at the extreme end of the hot-blast main away from the furnace, (2) at the hot-blast valve well on each stove, and (3) between the stove nearest the furnace and the bustle-pipe connection. The first two named showed practically the same temperatures on opposite sides of the hot-blast main connection, but the last showed a variation of at least 100° F. at all times.

We checked the quantity of wind discharged by each tuyere by determining the difference in pressure in a 36-in. length of the blow pipe. This was obtained by inserting a tube in the peep sight hole of the tuyere stock. This tube had two holes drilled 36 in. apart, to which were fitted two small pipes, to obtain the difference in pressure from one hole to the other. The differential pressure across these two small pipes were read from a mercury column. Not enough data have yet been checked to determine the value of these tests, but we believe that eventually they will be of some practical use.

The correct tuyere area for each different volume of blast blown has been a point on which many furnacemen disagree. One very good furnaceman told us that a figure of 6.75 sq. in. of area per 1000 cu. ft. of blast per minute was correct. Another man informed us that a constant of 6.25 sq. in. was better for his practice. These figures indicate that some furnacemen believe that the velocity of the blast at the nose of the tuyere must be held constant. We can best give our own views by a review of an experience. The blast volume had been decreased to 28,000 cu. ft. per min. from 38,000. This was the lowest point at which the wind had been held on the furnace at that time. The furnace had done excellent work on 38,000 cu. ft. per min. with twelve 5 by 12-in. tuyeres, so when the wind was lowered the new area was proportioned according to the constant-velocity theory in this manner:

$$38,000 \text{ cu. ft. per min.} = 12 \times 0.786 \times 5^2 = 236.0 \text{ sq. in.}$$

tuyere area [4]

$$28,000 \text{ cu. ft. per min.} = \frac{236 \times 28,000}{38,000} = 174.0 \text{ sq. in. tuyere area [5]}$$

Accordingly, nine 4 by 12-in. tuyeres were installed, making the area 172.2 sq. in. The furnace did not work smoothly and it required constant checking to keep her moving. The iron looked cold in the runner in spite of the fact that the analysis was within specifications. Some temperatures as low as 2500° F. were read on an optical pyrometer, whereas the iron normally ran around 2700° F. It was noticed that the 4-in. tuyeres were "dead" with very little action, while the 5-in. tuyeres showed normal movement of the coke. It was then that the thought occurred to us that the weight of the blast entering each tuyere was a factor as well as the velocity in producing normal tuyere action. A

review of Johnson's chapter⁸ on mechanical principles disclosed the fact that he was of the opinion that the energy of the blast jet was proportional to the square of the velocity. He said that "the energy of the blast jet also varies as the square of its velocity" and that "this energy represents the ability of the blast jet to overcome resistance in its line of action—in other words, its penetration." From this it seemed probable that the kinetic energy of the blast jet should be held constant for all wind volumes blown. We decided to solve for the value of this kinetic energy for our practice on 38,000 cu. ft. per min. wind, which was as follows:

Q_1 = volume of blast at 60° F. and 30-in. Hg = 38,000 cu. ft. per min.

P_1 = pressure at the bustle pipe = 14.1 lb. per sq. in.

T_1 = temperature of the blast at the bustle pipe = 1315° F.

M = weight of blast in lb. per sec.

S = specific volume of air at 60° F. and 30-in. Hg = 13.10 cu. ft. per lb.

$$\text{Then } M = \frac{Q_1}{60S} = \frac{38,000}{60 \times 13.10} = 48.1 \text{ lb. per sec.} \quad [6]$$

Allowing for a 1.5 lb. per sq. in. drop in pressure from the bustle pipe to the tuyeres:

$$P = P_1 - 1.5 = 14.1 - 1.5 = 12.6 \text{ lb. per sq. in.} \quad [7]$$

where P = the actual air pressure at the nose of the tuyeres in pounds per square inch. Allowing a 30° F. drop in temperature from the bustle pipe to the nose of the tuyeres:

$$T = T_1 - 30 = 1315 - 30 = 1285^\circ \text{ F.} \quad [8]$$

where T = the actual air temperature at the nose of the tuyeres in degrees F.

$$Q = \frac{Q_1}{60} \times \frac{T + 460}{60 + 460} \times \frac{P}{P + 14.5} = \frac{38,000}{60} \times \frac{1,285 + 460}{60 + 460} \times \frac{12.6}{12.6 + 14.5} =$$

$Q = 988$ where Q = actual volume of air at the nose of the tuyeres in cu. ft. per sec. [9]

$$A = \frac{12 \times 0.786 \times 5^2}{144} = 1.64 \text{ sq. ft.} \quad [10]$$

where A = free area of the tuyeres in square feet.

$$V = \frac{Q}{A} = \frac{988}{1.64} = 603 \text{ ft. per sec.} \quad [11]$$

⁸ J. E. Johnson, Jr.: Reference of footnote 4, 100.

where V = actual velocity of air at the nose of the tuyeres.

$$K = MV^2 = 48.1 \times 603^2 = 17.5 \times 10^6 \quad [12]$$

where K = a constant.

The conditions for 28,000 cu. ft. per min. were as follows:

$$Q_1 = 28,000 \text{ cu. ft. per min. at } 60^\circ \text{ F., } 30\text{-in. Hg}$$

$$P_1 = 12.8 \text{ lb. per sq. in.}$$

$$T_1 = 1400^\circ \text{ F.}$$

$$M = \frac{28,000}{60 \times 13.10} = 35.5 \text{ lb. per sec.} \quad [13]$$

$$P = 12.8 - 1.5 \times \frac{28,000^2}{38,000^2} = 12.0 \text{ lb. per sq. in.} \quad [14]$$

$$T = 1400 - 30 = 1370^\circ \text{ F.} \quad [15]$$

$$Q = \frac{28,000}{60} \times \frac{1,370 + 460}{60 + 460} \times \frac{12.0}{12.0 + 14.5} = 744 \text{ cu. ft. per sec.} \quad [16]$$

Solving for A :

$$K = \frac{M(Q)^2}{(A)} \quad [17]$$

$$A^2 = \frac{MQ^2}{K}$$

$$A^2 = \frac{35.5 \times 744^2}{17.5 \times 10^6} = 1.12$$

$$A = 1.06 \text{ sq. ft. or } 152.5 \text{ sq. in. tuyere area.}$$

The three 5 by 12-in. tuyeres were replaced by 4 by 12-in. tuyeres, making the total area 151.0 sq. in. The tuyeres were normal at once, and in a few days the furnace was working smoothly and the iron was hot enough.

The value for K at another plant was found to be 16.0 instead of 17.5, a difference that undoubtedly was due to the difference in coke.

THEORY AND PRACTICE ON SLOW-WIND OPERATION

If the above-mentioned fundamentals are complied with, the furnace should show a substantial decrease in fuel consumption and flue-dust losses, in spite of the fact that the radiation loss is a constant value per unit of time, and hence the percentage increases directly with the decrease in daily production.

We are fortunate in having the actual practice of two furnaces, B and C, the lines of which are shown on Figs. 6 and 7 respectively. The practice is charted on Figs. 8 and 9 respectively, and for convenience is tabulated in Table 4.

TABLE 4.—*Practice on Two Furnaces*

| Number of Months | Average Wind, M. Cu. Ft. per Min. at 60° F., 30-in. Hg | Average Tonnage, G.T. Pig per Day | Fuel Consumption, Lb. per G.T. Pig | | Flue Dust, Lb. per G.T. Pig | | Purch. Scrap Charged Lb. per G.T. Pig | Top Gas, Average CO ₂ , Per Cent |
|------------------|--|-----------------------------------|------------------------------------|--------------|-----------------------------|---------|---------------------------------------|---|
| | | | Coke | Fixed Carbon | Pro-duced | Charged | | |

FURNACE B

| | | | | | | | | |
|---|-------|-----|------|------|-----|-----|----|------|
| 4 | 20.87 | 347 | 1661 | 1439 | 20 | 20 | 24 | 16.1 |
| 4 | 38.87 | 592 | 1751 | 1523 | 165 | 183 | 39 | 15.3 |
| 4 | 51.82 | 734 | 1880 | 1627 | 271 | 245 | 19 | 13.8 |
| 1 | 60.50 | 811 | 1994 | 1727 | 361 | 361 | 7 | 13.6 |

Average ash in coke, 10.72 per cent; average sulfur in coke, 0.96 per cent; number gas samples taken, 58 (4-hr. samples)

FURNACE C

| | | | | | | | | |
|---|-------|-----|------|------|-----|---|---|------|
| 5 | 26.60 | 396 | 1818 | 1583 | 122 | 0 | 0 | 15.1 |
| 5 | 39.90 | 618 | 1869 | 1620 | 147 | 0 | 0 | 15.0 |
| 8 | 50.00 | 757 | 1899 | 1652 | 154 | 0 | 0 | 14.3 |
| 7 | 56.60 | 833 | 1949 | 1687 | 233 | 0 | 0 | 13.0 |

Average ash in coke, 9.83 per cent; average sulfur in coke, 0.91 per cent; number gas samples taken, 2082 (mostly snap samples)

The following gas samples (1017 in number) were taken at 9 in. from the inwall over a 12 months' period:

| WIND, CU. FT. PER MIN. | CO ₂ , PER CENT |
|------------------------|----------------------------|
| 50.0 | 9.2 |
| 37.0 | 13.6 |
| 25.5 | 14.5 |

The practice for each of these furnaces was selected from normal months during which no banking or blowing in was done, so as not to distort the results. The monthly practice data were averaged for months in which the average wind was approximately the same. A total of 13 months practice was used for furnace B and 25 months for furnace C. Little or no purchased scrap was used on either furnace during these months, the maximum amount for any one month being 46 lb. per G.T. pig for furnace B.

The curves are almost identical in shape, although furnace B had the better practice on low wind. This may be because furnace B had the larger stack, which would increase the time of gas-solid contact. Furnace C had the lower flue-dust losses on blast volumes averaging over 36,000 cu. ft. per min., though the fact that all the flue dust produced by furnace B was charged back "raw" greatly aggravated this condition.

No raw flue dust was charged back in furnace C. We also believe that the large inwall batter of furnace B (1.187 in. per foot) was partly responsible for the relatively large increase in flue-dust production with the greater blast volumes. The tonnage and top-gas CO_2 curves are practically identical.

Our reasons for the decrease in fuel consumption are twofold. First, the gas distribution through the stack is more uniform and free from channeling, particularly up the walls. This is evidenced by the CO_2

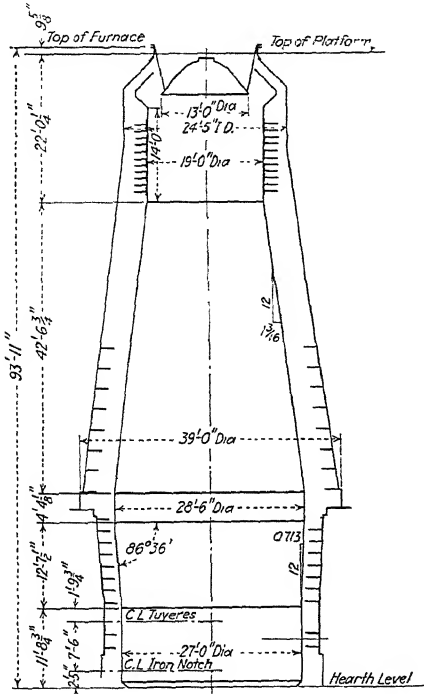


FIG. 6.

FIG. 6.—OUTLINE AND SECTION, FURNACE B.

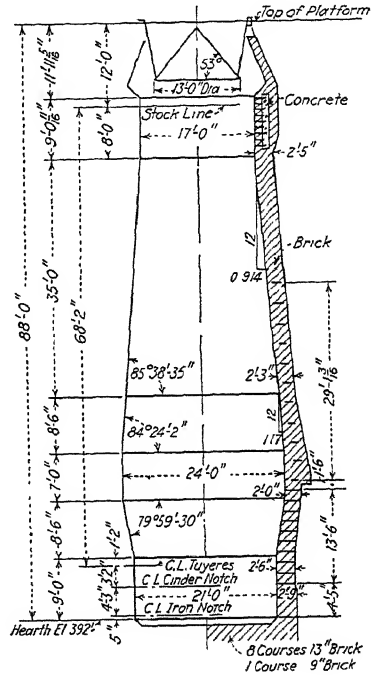


FIG. 7.

FIG. 7.—OUTLINE AND SECTION, FURNACE C.

curve at 9 in. from the inwall on furnace C. As the wind is decreased this curve shows an increase in CO_2 , until at very low wind the CO_2 at the inwall is nearly that of the average top gas, in spite of the channeling resulting from the effect of the batter and increased voids at the inwall. The other reason advanced for the lowering of the coke rate is that each particle of ore is subjected to the action of the reducing gases for a longer interval of time as the wind is lowered. The same holds true for each unit volume of CO gas in contact with the ore. J. E. Johnson, Jr.⁹ says: "A sufficient allowance of time for complete reduction of the

⁹ J. E. Johnson, Jr.: Reference of footnote 4, 305.

ore in each zone is an indispensable condition for maximum economy." Mr. Johnson also ran some experiments¹⁰ to determine the extent to which CO could be oxidized in the presence of iron ore at given temperatures. To quote:

After overcoming the worst of the difficulties in this determination, we were unable from lack of time to get a long series of these determinations, at different temper-

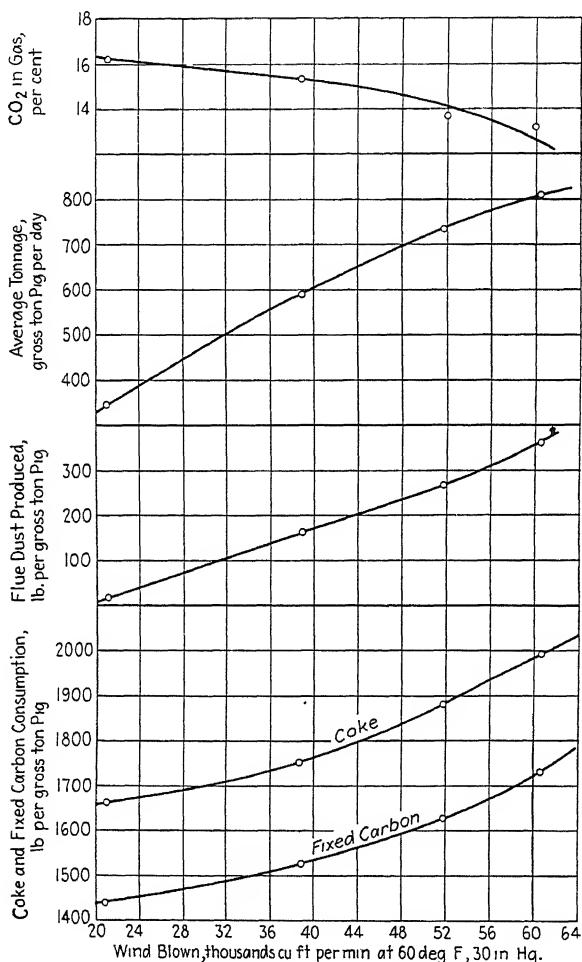


FIG. 8.—PRACTICE ON BLAST FURNACE B.

atures, as we had hoped, but we demonstrated by several runs that at a temperature of about 700° F. 62 per cent of CO₂ were in equilibrium with 38 per cent of CO. This means that *if sufficient time were allowed*, it would be possible to oxidize the top gases so that the CO₂ would hold this ratio to CO at this temperature. We also proved conclusively that the equilibrium percentage was much higher in CO₂ as the temper-

¹⁰Reference of footnote 4, 51.

ature rose. At 800° it is about 70 to 75 per cent, and at about 900° it is around 80 per cent CO₂, but these figures are not exact.

We believe that the principal reason for the great decrease in flue-dust production is the decreased velocity of the top gas at the stock line. It is generally conceded that the lifting effect on a given particle in a gas stream is proportional to the square of the velocity. As the velocity

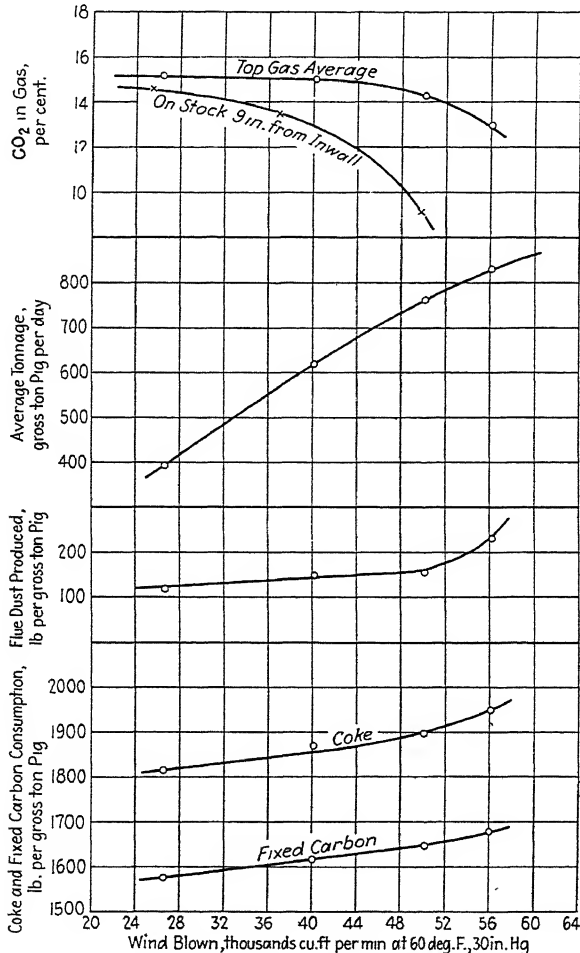


FIG. 9.—PRACTICE ON BLAST FURNACE C.

of the gas varies directly with the wind volume and the tonnage varies in nearly the same manner, the result is that the amount of flue dust produced per gross ton of pig is almost in direct proportion to the blast volume. This fact is borne out by the curves of Figs. 8 and 9, in which the flue-dust curves are nearly straight lines. The decreased channeling effect of lowered blast volumes also affects the flue-dust production, in

that the mean value of the squares of the velocities at each unit area of the stock line is lower.

The question may arise as to how fast the wind can be increased or decreased on a furnace without seriously affecting the operation of the furnace and the quality of the product. Our experience is that the wind can be increased at the rate of 2000 to 2500 cu. ft. per min. per 24 hr. and decreased at twice this rate, provided the walls are fairly clean and that the correct tuyere size is used at all times. Where the wind was increased substantially, the practice for the first month of operation on the higher blast volume has been unsatisfactory. At the end of this first month the furnace was generally operating normally.

The question of just how low it is possible to go with the wind on a given furnace is often asked. It is our opinion that the minimum size of tuyeres would be the limiting factor. It would probably be possible to operate on 2-in. tuyeres, but we feel that with a smaller size great difficulty would be experienced. Another consideration is that the bottom and walls of the hearth tend to build up on low wind. It is altogether possible that the bottom might build up to the point where the product could not be extracted from the tapping hole. The fuel-consumption curves of Figs. 8 and 9 show that the rate of decrease of coke consumption is lower with each corresponding decrease of wind. This implies that the coke rate will reach a minimum at some low volume and then increase as the wind volume is lowered still more. This point is where the fuel economies affected by the low wind and resulting efficient gas-solid contact exactly balance the ever-increasing radiation and cooling-water loss.

The equation for the curve of fixed carbon vs. wind volume for furnace B is as follows:

$$C = 0.0923B^2 - 0.653B + 1385 \quad [18]$$

where C = fixed carbon consumption, lb. per G.T. pig,

B = blast volume, M. cu. ft. per min.

The first derivative of this expression is

$$D_B C = 0.1846B - 0.653 \quad [19]$$

Equating $D_B C$ to zero, gives:

$$0 = 0.1846B - 0.653 \quad [20]$$

$$B = 3.53$$

Thus the blast volume to provide the minimum coke rate of furnace B is 3530 cu. ft. per min. This would provide a minimum fixed carbon consumption of 1384 lb. per G.T. pig or a coke rate of 1596 lb. per G.T. pig.

The equation for the same curve for furnace C is as follows:

$$C = 0.0167B^2 + 1.667B + 1527 \quad [21]$$

The first derivative of this expression is:

$$D_B C = 0.0334B + 1.667 \quad [22]$$

Equating value of $D_B C$ to zero,

$$\begin{aligned} 0 &= 0.0334B + 1.667 \\ B &= -49.90 \end{aligned} \quad [23]$$

From this it is obvious that this curve does not have a minimum point on the right side of the C axis, hence zero blast volume would provide a fixed carbon consumption of 1527 lb. per G.T. pig and a coke consumption of 1760 lb. per G.T. pig. The flue dust would reach zero production at zero wind.

CONCLUSIONS AND RECOMMENDATIONS

We are convinced that practically all blast-furnace operators in this country were overblowing their furnaces prior to the depression by reason of the data set forth. There is one particular volume of blast for each furnace that will produce a certain tonnage of iron at a cost lower than the cost will be at any other blast volume, with the same raw materials, prices, labor costs and equipment. It is the duty of each operator to determine this point on each furnace under his supervision, and thus arrive at the most economical rating for each size of furnace operating under the given set of conditions. Thus when a furnace is to be relined or rebuilt the operator will know the size furnace to build in order to produce the tonnage required, in the same manner that an electrical engineer determines the size of motor to be installed when he is acquainted with the average, minimum and maximum load and speed requirements.

From the above it is evident that the large-hearth, high furnace with the wide top is the best for Lake ore practice. This large furnace is very flexible as far as tonnage is concerned, and is more economical to operate when the conservation of raw materials is considered. Furnace B, for instance, with a 27-ft. hearth produced a minimum of 347 gross tons of pig per day over a four-month period, and made as high as 811 gross tons pig per day. It is believed by the operators of this furnace that it is possible to produce 1200 gross tons of pig per day. This is a production regulation of $\frac{100(1200 - 347)}{1200}$, or 71.2 per cent.

The decreased coke rates and flue-dust productions on slow wind are due partly to the decreased volume of blast and partly to the slowing up of the descent of the column of stock. It is impossible to determine, at the present time, the relative effect each of these conditions has on the increased economical working of the furnace, but it is our opinion that the lower blast volume has the greater effect. This would mean that the much talked of practice of increasing the oxygen content of the blast

might be developed, in order to produce the required tonnage of iron and still keep the total volume of blast down low. Thus for furnace B:

Required production = 811 G.T. per day

Coke rate using normal air = 1994 lb. per G.T. pig

Fixed carbon rate normal air = 1727 lb. per G.T. pig

Blast volume normal air = 60,500 cu. ft. per minute.

It is desired to produce 811 gross tons of pig per day on 50 per cent of the normal wind, which equals 30,250 cu. ft. per min. Assuming that the effect of the decreased nitrogen content of the blast would balance that of the normal movement of stock, we find in the curves on Fig. 8 that the following is true for a wind volume of 30,250 cu. ft. per min.:

Coke rate = 1700 lb. per G.T. pig

Fixed carbon rate = 1478 lb. per G.T. pig

$$\text{O}_2 \text{ required} = \frac{811 \times 1478 \times 58 \times .21}{1440} = 10,160 \text{ cu. ft. per min.} \quad [24]$$

$$\text{O}_2 \text{ content of blast} = \frac{100 \times 10,160}{30,250} = 33.5 \text{ per cent} \quad [25]$$

$$\begin{aligned} \text{O}_2 \text{ required over that present in normal air} &= \frac{33.5 - 21.0}{100} (30,250) \\ &= 3780 \text{ cu. ft. per min.} \quad [26] \end{aligned}$$

TABLE 5.—*Comparison of Set-ups*

| Item | Unit | Present | Proposed | Savings |
|--------------------------------------|------------------|---------|----------|---------|
| Production | G.T. per day | 811 | 811 | 0 |
| Coke rate..... | Lb. per G.T. | 1,994 | 1,700 | 294 |
| Flue dust..... | Lb. per G.T. | 361 | 92 | 269 |
| Volume blast..... | Cu. ft. per min. | 60,500 | 30,250 | 30,250 |
| Volume normal air blast... | Cu. ft. per min. | 60,500 | 26,470 | 34,030 |
| Volume O ₂ additional . . | Cu. ft. per min. | 0 | 3,780 | 3,780 |
| Blast pressure... .. | Lb. per sq. in. | 19 | 13 | 6 |

Table 5 gives a brief summary of the two set-ups. The savings on an installation to produce the required oxygen can be calculated from Table 5 for each individual case.

Another advantage in favor of such an installation would be that a constant blast temperature could be used at all times, as the quality of the product could be controlled by variation of the oxygen content of the blast. This would permit the stoves to operate at maximum capacity and efficiency.

It is possible to use heavy batters on the furnace inwall with low volumes of wind, but when high volumes are blown we believe that this reacts unfavorably on the furnace practice. Too small a batter retards the descent of the stock, and this often results in the "hanging" or

uneven movement of the charge. We may classify the inwall batters roughly as follows:

1. Light batter, under 0.8 in. per foot.
2. Medium batter, from 0.8 to 1.0 in. per foot.
3. Heavy batter, over 1.0 in. per foot.

We favor the medium batter in the range of from 0.8 to 0.9 in. per foot.

More research and experimentation should be done on the gas flow in the blast furnace, in order to determine the location of the greatest channeling. Once this has been satisfactorily determined for the conditions present, then intelligent effort can be made to correct the bad features of the gas flow by changes in filling or design of the top-charging mechanism and furnace lines.

Additional investigations, similar to those of the Bureau of Mines, should be made with models. We suggest that, when the shaft of the model furnace is full, the material be extracted from holes located in the walls and at the bottom of the model, until the furnace is entirely filled with stock charged at a constant stock level. This should simulate the descent of stock under actual operating conditions. The condition of the stock at any level in the model can then be investigated and conclusions drawn therefrom. In addition to the variables already checked by the Bureau of Mines, the effects of changes in design of the charging apparatus and furnace lines should be determined.

ACKNOWLEDGMENTS

The author wishes to acknowledge the help received from the officials and men of the Republic Steel Corporation in the form of cooperation, aid and constructive criticism. These include Mr. H. B. Carpenter, Manager of the Youngstown District, Mr. B. W. Norton, Superintendent of Blast Furnaces and Coke Works for the Youngstown District, who have given help, ideas and encouragement in the investigations and preparation of this paper; Mr. J. H. Slater, Superintendent of the Blast Furnaces and Coke Works, and Mr. G. F. Kerwin, Superintendent of the Blast Furnaces, of the Warren District, who have been generous in their contribution of ideas and facts on the very excellent practice of their large furnace; Mr. A. J. Macdonald, Mr. W. O. Bishop, Mr. O. E. Moff and many others of the Youngstown Blast Furnace Department, for their personal help and suggestions.

The author is especially indebted to Mr. S. P. Kinney, formerly of the Bureau of Mines, for the inspiration of his interest, criticism and ideas. Mr. T. L. Joseph and other Bureau of Mines men have been very helpful in their donation of ideas and facts, gathered from their reports and personal contacts.

Acknowledgment is made to many men of the Youngstown Sheet and Tube Co. organization. In the Campbell plant, Mr. C. H. Heist, Assistant General Superintendent, Mr. B. M. Stubblefield, Superintendent of Blast Furnaces and the Coke Plant and Mr. D. P. Cromwell, Superintendent of Blast Furnaces, have given helpful and constructive aid. Mr. C. M. Horan, Assistant Superintendent of Blast Furnaces, has devoted a great deal of time and thought to much of the work described in this report. Mr. Otho Kay and Mr. J. F. Agerter have also been helpful in their accurate compilation of records. Mr. G. W. Williams, Superintendent of Blast Furnaces and Coke Works, and Mr. Reed Lewis, Superintendent of Blast Furnaces, both of the Indiana Harbor Works of the Youngstown Sheet and Tube Co., have provided much information on low-wind practice.

DISCUSSION

(C. B. Murray presiding)

T. L. JOSEPH,* Minneapolis, Minn (written discussion).—Mr. Rich has made a valuable contribution in reporting his observations on slack-wind practice and the results of his experiments in correlating methods of filling and gas distribution near the stock line. It is desirable to have a report to preserve the results of the intensive furnace practice which has been necessary during the depression.

The adjustment of tuyere area is an important problem that arises when the rate of blowing is varied widely. It is generally thought that tuyere area should be adjusted to give proper penetration. That is, the air blast should penetrate a certain distance beyond the nose of the tuyeres. The mechanical agitation produced in front of the tuyeres by the force of the blast seems to be more important than the matter of penetration, although the two are interrelated. If the air blast produces a lively tuyere, the coke is constantly shifting, which prevents the chilling of ash-coated pieces directly in front of the tuyeres. Coke particles covered with ash or slag do not remain directly in front of a lively tuyere except for a short time. They shift around, facilitating removal of the ash and slag, and when directly in front of the tuyere present clean surfaces. On the contrary, if the air blast does not produce this desirable mechanical stirring, the result is dead tuyeres, referred to on page 37 of Mr. Rich's paper.

Whether we consider tuyere action from the standpoint of mechanical agitation produced by the blast or from the standpoint of penetration, the kinetic energy of the blast seems to be the proper basis upon which to adjust the tuyere area according to the rate of blowing. The constant given on page 39 and the method by which an operator can adjust the tuyere area should be very valuable.

The chief value of experiments with models is in picturing and analyzing the various factors involved and in suggesting promising leads for tests on full-scale equipment. It is encouraging therefore to learn that results of model studies made by the Bureau of Mines were, in general, confirmed by actual furnace tests. The results of gas samples removed 9 in. from the inwall, given in Tables 2 and 3, show very definitely that the gas distribution near the stock line can be changed decidedly

* Supervising Engineer, North Central Experiment Station, U. S. Bureau of Mines.

by varying the size of the ore charge. In the straight section of the furnace near the stock line, it is possible to get a fairly accurate picture of the arrangement of the ore and the coke layers as given in Fig. 4. Below the straight section, the effect of the batter and mixing of the layers due to unequal rate of stock descent complicate the situation. Kinney's surveys across a plane 3 ft. below the actual stock line in the straight section and across a plane 11 ft. below the actual stock line or a few feet below the straight section show that the batter had produced a section of low CO_2 content extending inward about 2 ft. from the inwall. The diameter at the 11-ft. plane was 17 ft. 6 in. compared to 17 ft. for the stock line or straight section. The cross-sectional area was therefore about the same in both planes, so it appears that the layered arrangement was much the same on the lower plane as at the stock line. I am inclined to attribute the open area near the inwalls in the tapered section to the effect of the batter in retarding the packing of the stock near the walls rather than to the absence of ore as pictured in Fig. 5. There would, it seems, be some ore at the inwall at an elevation 21 ft. 7 in. below the stock line unless it has been blown out as dust.

The data presented in Figs. 8 and 9, showing lower coke consumption on slow rates of blowing, are very interesting. Since, as Mr. Rich points out on page 39, radiation and cooling-water losses are approximately constant, lower fuel consumption on slack wind means that carbon is used more efficiently at slower rates of blowing. The top section of Fig. 9, showing greater difference in the CO_2 content of the gas 9 in. from the wall, as compared to the top gas as the wind was increased, indicates more uniform gas distribution for slower rates of blowing. Less channeling and generally lower gas velocities are no doubt responsible for decreased production of dust as the rate of blowing decreases. In view of faster stock travel in some parts of the furnace, the longer time of contact seems equally important, however, to gas distribution in facilitating more complete reduction and tending towards more efficient use of carbon.

The operation of a blast furnace cannot be reduced to curves and mathematical formulas. Mr. Rich's paper shows, however, that by systematic effort and study conclusions can be reached that will be an important supplement to the experience, ingenuity, and skill of the operator and advance the general understanding of the smelting process.

F. W. DAVIS,* Milford, Del. (written discussion).—Mr. Rich has made a valuable contribution to our knowledge of blast-furnace technology. His paper is of particular interest to me in that it helps to explain a seeming discrepancy between practice and thermal calculations which I encountered about three years ago, when I was retained on a matter involving the operation of a semi-commercial (10-ton) blast furnace. During the period of operation, at about 3 o'clock one morning, I was called from bed and informed that, presumably through an error in filling, the hearth of the furnace had become sufficiently chilled to prevent tapping and that the tuyeres were rapidly becoming black. By the time I reached the plant, all tuyeres were black and the iron pipe hot-blast stove had failed under the increased blast pressure.

There was a large supply of oxygen in cylinders available and I decided that the time was opportune to put to test some of my ideas as to the benefits to be expected from the use of an oxygen-enriched blast. I had a manifold connected to the hot-blast main and by regulating the time of discharge of cylinders increased the oxygen content of the blast by about 2 per cent. The effect was apparent almost instantly. The tuyeres brightened up, the back-pressure on the blast main was reduced and within less than 30 min. the furnace was successfully tapped. The oxygen enrichment was then reduced to approximately one per cent, which appeared sufficient to maintain

* Consulting Engineer.

cold-blast operation until the coke blank that had been charged directly after the irregular operation had been noticed had reached the smelting zone.

At the conclusion of this trial I tried to justify the results actually obtained from the oxygen enrichment by thermal calculations, but failed. Such calculations as I could make with the rather meager data obtained indicated the necessity for a greater oxygen enrichment than was used or as a matter of fact was available. I concluded

therefore that the thermal analysis, based on our present knowledge of smelting reactions, is inadequate to fully define the effects of oxygen enrichment.

In his analysis of the effect on operation of decreasing the blast volume by means of decreasing the nitrogen content of the blast, I believe Mr. Rich has overlooked the thermal effect in the smelting zone of this proposed practice and its consequent effect on smelting capacity.

There are three methods by which changes may be effected in smelting economy by manipulation of the blast. Sensible heat may be added to the blast by hot-blast stoves. The energy of the blast may be increased by increasing the partial pressure of the oxygen through oxygen enrichment. The volume of the blast may be regulated.

An increase in blast temperature increases the amount of high-temperature heat available for smelting per unit of coke. A decrease in blast volume cannot effect an increase in available smelting heat, but by causing a more complete preparation of the burden in the shaft section reduces the thermal

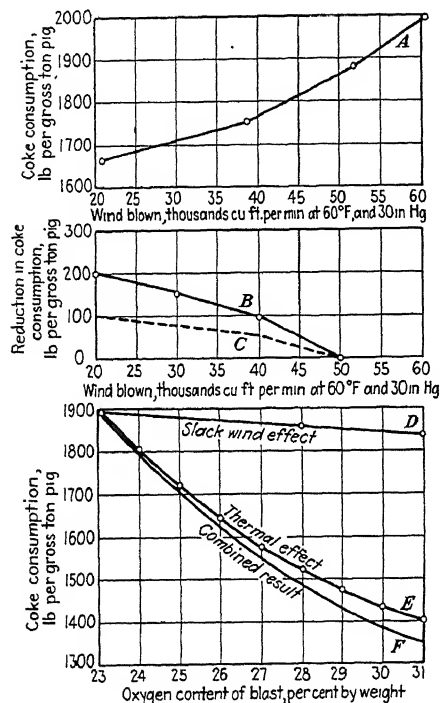


FIG. 10.

requirements. The addition of oxygen to the blast increases the amount of high-temperature heat available and at the same time, by virtue of the decreased volume, decreases thermal requirements.

From a thermal standpoint alone, increasing the oxygen content of the blast is in effect decreasing the quantity of nitrogen that is forced through the furnace. Each pound of nitrogen heated to blast temperature of, say, 1200° F. and introduced into the furnace as blast adds 289 B.t.u. to the heat of the smelting zone. Since it leaves the smelting zone at approximately 2800°, the nitrogen removes 727 B.t.u. per pound. The net result therefore is a loss in available smelting heat of 438 B.t.u. for each pound of nitrogen in the blast.

For the purpose of illustrating the difference in magnitude of the thermal effect and the slack-wind effect of nitrogen removal, I have prepared Tables 6 and 7 and Fig. 10. The calculations are based on data obtained from a Chicago district furnace operating on Lake ores. At the time the data were taken the furnace was producing 717 tons of pig per day, with a coke consumption of 1894 lb. per ton; 50,000 cu. ft. of air was blown per minute at a mean blast temperature of 1160° F.

Table 7, based on the values developed in Table 6, shows the change in available smelting heat and coke consumption resulting from the thermal effect only of the

TABLE 6.—*Heat Balance of Smelting Zone per 100 Lb. Coke*

| HEAT TO HEARTH | | B.T.U. |
|---|--|---------|
| 1. Heat in oxygen from blast, 87 lb. at 1160° F. | | 21,228 |
| 2. Heat in nitrogen from blast, 290 lb. at 1160° F. | | 80,620 |
| 3. Heat in water vapor from blast, 3.8 lb. at 1160° F. | | 2,010 |
| 4. Heat in total carbon to hearth, 81.5 lb. at 2740° F. | | 88,020 |
| 5. Heat in O ₂ content of FeO, SiO ₂ etc., 12 lb. at 2740° F. | | 7,452 |
| 6. Heat of combustion of carbon oxidized in hearth, 76.8 lb. | | 336,000 |
| 7. Total heat generated in hearth and bosh section. | | 535,330 |
| HEAT REMOVED FROM HEARTH | | |
| 8. Heat in CO to shaft, 179.2 lb. at 2800° F. | | 130,278 |
| 9. Heat in nitrogen to shaft, 290 lb. at 2800° F. | | 210,830 |
| 10. Heat of decomposition of H ₂ O in blast, 3.8 lb. | | 21,974 |
| 11. Heat in H ₂ to shaft, 0.42 lb. at 2800° F. | | 4,213 |
| 12. Radiation and conduction. | | 22,525 |
| 13. Heat imparted to cooling water. | | 22,525 |
| 14. Total heat removed from hearth and bosh section. | | 412,345 |
| 15. Heat available for smelting, (No. 7—No. 14) | | 122,985 |
| HEAT UTILIZED IN SMELTING 118.3 LB. PIG IRON | | |
| 16. Heat imparted to slag, 47 lb. | | 8,131 |
| 17. Latent heat of iron, 111.3 lb. | | 14,024 |
| 18. Heat in carbon in iron, 4.7 lb. | | 5,076 |
| 19. Heat of reduction of P, 0.2 lb. | | 2,122 |
| 20. Reduction of Mn, 0.7 lb. | | 2,082 |
| 21. Reduction of Si, 1.4 lb. | | 17,640 |
| 22. Removing 10 lb. O ₂ from iron. | | 73,910 |
| 23. Total heat utilized. | | 122,985 |

oxygen enrichment. The change in blast volume is also noted, it being assumed that the rate of delivery of oxygen to the furnace remains constant. No credit has been taken for the reduced amount of moisture in the blast. Since rectified air is moisture-free, the moisture content of the blast will be reduced in proportion to the oxygen enrichment.

TABLE 7.—*Thermal Effect of Increasing the Oxygen Content of the Blast*

| Oxygen Content of Blast, Per Cent | Nitrogen in Hearth Gas, Lb. | Net Heat Removed From Smelting Zone by Nitrogen, B.t.u. | Increase in Available Smelting Heat | | Coke Required per Gross Ton Pig, Lb. | Blast, Cu. Ft. per Min. |
|-----------------------------------|-----------------------------|---|-------------------------------------|----------|--------------------------------------|-------------------------|
| | | | B.t.u. | Per Cent | | |
| 23.1 | 290 | 130,210 | 0 | 0 | 1894 | 50,000 |
| 24 | 276 | 123,924 | 6,286 | 5.1 | 1805 | 48,096 |
| 25 | 261 | 117,189 | 13,021 | 10.6 | 1721 | 46,050 |
| 26 | 248 | 111,352 | 18,858 | 15.3 | 1646 | 44,270 |
| 27 | 235 | 105,515 | 24,695 | 20.0 | 1579 | 42,490 |
| 28 | 224 | 100,576 | 29,634 | 24.1 | 1525 | 41,010 |
| 29 | 213 | 95,637 | 34,573 | 28.1 | 1478 | 39,500 |
| 30 | 203 | 91,147 | 39,063 | 31.7 | 1436 | 38,150 |
| 31 | 194 | 87,106 | 43,104 | 35.0 | 1404 | 36,900 |

Although I appreciate that the figures obtained by Mr. Rich on the effect of blast volume on coke consumption apply only to the particular practice noted, in order to show the relative magnitude of the two effects, the thermal effect of nitrogen elimination and the mechanical effect due only to the reduction in blast volume, I have combined his results from furnace B with the thermal data of Table 7 in Fig. 10.

Curve A was plotted from Mr. Rich's data on coke consumption as a function of blast volume as found from tests on furnace B.

Curve B shows reduction in coke consumption as a function of blast volume, with 50,000 cu. ft. of air per minute as a reference base.

Curve C shows one-half of the reduction in coke consumption, assumed to be the direct result of the reduction in gas velocity.

Curve D shows the "slack-wind" effect as a function of oxygen content of blast. The values being taken from curve C.

Curve E, plotted from Table 7, shows the thermal effect in the smelting zone of nitrogen elimination.

Curve F, a summation of curves D and E, indicates the combined saving from the thermal and slack-wind effects.

W. A. HAVEN,* Cleveland, Ohio.—Mr. Rich was born in the twentieth century and perhaps I am not of the same generation as Mr. Sweetser, but I served with the men who have had charge of blast furnaces for the last 25 years and I am inclined to take exception to any inference that they have been working in the dark and have not been making the best of well established or even recently established principles.

Mr. Rich's paper apparently did not register on many of us certain features in which it is particularly impressive. First of all, Mr. Rich has brought out something which I believe has never been touched upon before in any of these technical meetings, which has to do with the volume of blast at the tuyeres. Mr. Rich's experience has evidently indicated that not only the velocity of blasts at the tuyeres has a tremendous bearing on the size of the tuyere that should be used, but also the energy of the wind going into the tuyeres. I recommend to your attention that feature of Mr. Rich's paper.

A second feature of the paper is simply more or less of an observation upon furnace practice, but certainly one to which everyone should give considerable attention. It is the evidence very clearly brought out in the depression period, when slack blast was practiced, showing that the making of low costs was very closely associated with the low velocity of the gases traveling through the furnaces. It was stated by one discussor that the management would not stand for blowing a 1200-ton furnace at 500-ton rate. I think the management not only would stand for it but would be glad to get 500 tons at low cost with a 1200-ton furnace, when there was no market for the other 700 tons.

Very much to our surprise, the actual cost at that rate of production was lower than the cost at the rate of 1200 tons, and certain lessons are to be drawn from that. Mr. Rich has pointed them out. If you have a furnace of 1000 tons capacity and other conditions around the steel plant enable you to operate at a 500-ton rate, there is nothing particular to be concerned about except that you have not enough business to run at 1000 tons; because your actual operating cost may be as little or less as when you were operating at that speed. And in this connection I want to get back to the theme of these remarks—that the operators having charge of the furnaces during these trying times have shown their ability to meet the situation by accomplishing so much even under conditions where they could not make the full tonnage designed for.

* Vice President, Arthur G. McKee & Co.

Blast-furnace Fuels—Anthracite Coal

BY RALPH H. SWEETSER,* MEMBER A.I.M.E.

(New York Meeting, February, 1935)

IN these days of the almost exclusive use of byproduct coke as the blast-furnace fuel in this country, it may seem out of place, and smacking too much of reminiscence, to say anything about the use of anthracite coal for blast-furnace fuel. Viewed in the light of present day research and of developments in alloy steel, some observations seem appropriate regarding this raw material that played such an important part in the development of the iron and steel industry during 50 years of the past century. The research work of that period, in which the whole iron and steel industry was revolutionized, passing from wrought iron to steel and from charcoal to three new mineral fuels for blast furnaces, was done chiefly in the full-sized plants of that day; and it was done largely by the ironmasters themselves. The laboratory had not become a part of the ironworks, and scientific instruments were lacking around the blast furnaces; "rule o' thumb" and erroneous theories prevailed—and have not yet all been eliminated. The recent interest in meteoric iron in connection with nickel steels and other alloys proves that it is worth while to search for the reasons for excellence and the causes for failures in the metallurgy of bygone days.

Turner¹ gives the reasons why the blast furnace of Dr. F. W. Geissenhainer on Silver Creek, Schuylkill County, Pennsylvania, about 10 miles northeast of Pottsville, was operated successfully with anthracite² in August and September, 1836, and why several other attempts failed. It has taken a long time for us to find out that there are great differences in the behavior of anthracites from the several parts of the anthracite region, as well as differences in coking coals from the bituminous fields.

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¹ H. G. Turner: Anthracites and Semianthracites of Pennsylvania. *Trans. A.I.M.E.* (1934) **108**, 330.

² J. M. Swank: Iron in All Ages. 1892.

ANTHRACITE AND THE A.I.M.E.

Many of the founders of A.I.M.E. were closely connected with the anthracite industry, and others were actually engaged in an iron industry that was built up on anthracite as the chief fuel. At that time, and for a few years afterwards, the bulk of pig iron made in this country was from furnaces using anthracite exclusively as the fuel. The TRANSACTIONS of the two decades following the beginning of the Institute in 1871 contain many papers on the operation of anthracite blast furnaces, including papers on how to overcome the furnace troubles incident to the use of anthracite, and to the blast-furnace practice of those days.

A good description of the blast-furnace practice of the 20-year period from 1855 to 1875, is given by Prof. John A. Church.³ One glance at the table on page 223 of that paper is enough to convince a blast-furnace man that the furnace troubles of that period were not all caused by the anthracite. For instance, the average amount of ore per ton of pig iron for 20 years was 2 tons (gross) and 667 lb., and the amount of limestone used per ton of pig iron was 1 ton and 969 lb. No wonder that it took 2 tons and 206 lb. of anthracite to make a ton of pig iron! Such a blast-furnace practice accounts for the mountains of slag that used to be so common in the Lehigh and Schuylkill valleys. The remarkable thing about this low-grade ore (about 41 per cent iron) was that the average cost delivered was over 10¢ per unit, \$4.10 per ton, at a time when the anthracite coal had a delivered cost of only \$3.71 per gross ton.

In volume 8 of the TRANSACTIONS is the story of the unique experience of John Birkinbine, who, in 1879, used charcoal, beehive coke and anthracite, one at a time, in the Pine Grove (Pa.) furnace.

SOME PECULIAR QUALITIES OF ANTHRACITE

Dr. Henry M. Howe recognized some of the peculiar advantages of anthracite as a blast-furnace fuel, and said⁴ that:

Incandescent anthracite reaching the tuyeres in the normal way reaches the temperature of 3404° C. on complete combustion to CO₂ and H₂O, and 2182° C. on subsequent reduction to CO and H. Fine anthracite blown through the tuyeres reaches 3389° C. on complete combustion to CO₂ and H₂O and 2114° C. on subsequent reduction to CO and H.

Dr. Howe further says that:

The most beautiful way of suddenly raising the temperature of the crucible would be to increase the proportion of O in the blast. The great amount of N in the blast has a most powerful effect in dragging down the temperature, forming, as it does, the great bulk of the products of combustion.

³ J. A. Church: Blast Furnace Statistics. *Trans. A.I.M.E.* (1875-76) 4, 221-226.

⁴ H. M. Howe: A Suggested Cure for Blast Furnace Chills. *Trans. A.I.M.E.* (1882-83) 11, 453.

The only practical application of oxygen to the blast of an anthracite blast furnace as suggested by Dr. Howe, as far as I am aware, was when J. E. Thropp, Jr. and I applied it to one of the Hellertown furnaces of The Thomas Iron Co., in 1916. Mr. Thropp had telephoned me early one morning that the furnace had made a heavy slip in the night and had filled the hearth with cold stock; that all the tuyeres were cold and no sign of fire inside the furnace at the tuyeres. I called up The Bethlehem Steel Co. and asked for a truckload of oxygen in tanks, and this was at the furnace when I arrived.

It surely was a cold furnace, with the engines barely turning over. When we told the foreman what we intended to do, he and all the furnacemen ran out of the cast house, leaving Mr. Thropp and me to apply the oxygen. The response was almost immediate, and soon the tuyere was white hot inside the furnace; and gradually other tuyeres were opened with the oxygen.

It is reasonable to expect that a larger percentage of anthracite will reach the tuyeres than of any other blast-furnace fuel, and that there will be less of the so-called "solution loss" in the upper regions of the furnace. There is, however, one characteristic of anthracite different from those of coke that may have some bearing on the total percentage of anthracite that reaches the tuyeres, and that is the amount of volatile matter in the natural fuel. The volatile matter in anthracite is of great advantage in the top of the furnace, in that it cools down the top gases to a greater extent than can be accounted for by the absorption of heat by the double weight per cubic foot of the anthracite dumped into the top of the furnace as compared with the weight of the fuel unit of coke. In a laboratory test I discovered that at the temperature of the top of a blast furnace there are endothermic reactions in anthracite that will take heat from the surrounding material, thus cooling the top gas to a greater extent than coke can cool it.

SIZE OF ANTHRACITE FOR BLAST FURNACES

The anthracite coal usually shipped to blast furnaces for fuel was "lump," which was everything over 7 in., and in those days the furnacemen called for "man size" limestone and ore, which meant lumps of all materials as big as one man could lift into his buggy. This was another erroneous theory of "keeping an open furnace" with the big lumps. The early anthracite furnaces had 3-in. tuyeres, so it is no wonder that it took two or three days for a change in the burden to come down to the tuyeres. Even in 1898 the standard size for anthracite tuyeres was 5 in., as quoted above from the paper of John Hartman. In 1886 the use of "steamboat" size was used with improved results, according to John Birkinbine,⁵ who made the following observation:

⁵ J. Birkinbine: *Trans. A.I.M.E.* (1886) 154.

A still further reduction in size will, it is believed, be advantageous by offering greater surface exposure, but at the expense of increased blast pressure; and the suggestion is offered, that in a plant specially equipped to use anthracite coal in small pieces results may be obtained which will demonstrate its real value as a fuel for blast furnaces.

In negotiating a contract for anthracite coal for the Alburtis furnaces of The Thomas Iron Co., in 1915, I tried to get broken (through $4\frac{3}{8}$ in. on $3\frac{1}{4}$ in.) or egg (through $3\frac{1}{4}$ in. on $2\frac{7}{16}$ in.), but the coal company would not listen to it, and we had to accept steamboat (through 7 in. on $4\frac{3}{8}$ in.), which is the sized recognized by Johnson (p. 184) as the anthracite for blast-furnace fuel. With very few exceptions, lump coal and steamboat coal were the sizes of anthracite used throughout the anthracite period of blast-furnace operation in this country.

In their paper on combustion of coke in blast-furnace hearth, mentioned above, Perrott and Kinney draw certain conclusions and quote Royster as follows: "combustion at the blast velocity obtaining in the furnace probably takes place on the exposed peaks of the cell walls, making a porous coke present less effective surface for combustion than a dense coke." This is at variance with the statement of Forsythe⁶: "a porous fuel will present more surface to the action of the blast than a dense one, and therefore facilitates and hastens combustion." Forsythe further says that, "a fuel which changes its shape in the furnace, either through being crushed or through softening under action of heat is undesirable." Anthracite is practically all "surface" when it reaches the tuyeres and has not changed its shape. Birkinbine said (reference of footnote 5):

If, as seems to be demonstrated, fuels rank in value in proportion to their surface exposure, charcoal is superior to coke, and coke excels anthracite, as a blast fuel; but as higher pressure of blast increases the value of coke as a fuel, so a further intensity augments the results with anthracite.

When we consider that the respective weights per cubic foot of the three fuels, charcoal, anthracite and coke, varied as much as 366 per cent, we can see what difficulties accompanied the transition from charcoal furnace practice to that of anthracite and of coke. In 1875, Prof. John A. Church wrote: "It seems to me that the secret of working the Eastern magnetites with anthracite coal has not been found." In comparing the excess of 25 to 30 per cent anthracite per ton of pig iron with the coke per ton of pig on the other side of the Atlantic, he said that the most experienced iron men of this country seem to think that the large requirement of fuel was a necessity inherent to anthracite coal, and added (reference of footnote 3): "the 'reason why' for this great consumption of anthracite

⁶ R. Forsythe: The Blast Furnace and the Manufacture of Iron 64. 1922.

appears to me to be one of the great questions of metallurgical practice in America."

TABLE 1.—*Weight of Blast-furnace Fuels*

| | WEIGHT OF 1 Cu. Ft., Lb. | | WEIGHT OF 1 Cu. Ft., Lb. |
|---------------------|-----------------------------|----------------|-----------------------------|
| Anthracite..... | 55 to 66 | Beehive coke.. | 25 to 31 |
| Byproduct coke..... | 28 to 35 | Charcoal | 18 to 18½ |

Those of us who went through the agony of using some of the early byproduct cokes shipped to blast furnaces from coke ovens that were primarily operated to furnish gas and other byproducts, in big lumps and over-coked and water-soaked from being quenched on a platform with a hose, can appreciate in a small degree, the drastic changes in blast-furnace practice necessary to get results with the new mineral fuels, anthracite, block coal and beehive coke, after two centuries of nothing but charcoal for blast-furnace fuel. (See comparison of weights of fuels in Table 1.) Those pioneering ironmasters did not have the facilities that furnacemen of today have at their command; but, unless we make further research into "the mystery or only true principle and manner" (to quote Dr. Geissenhainer) of the crucible of the modern blast furnace, the metallurgists of the future will have just cause to criticize us for not making proper use of the many opportunities that are now within our grasp.

ANTHRACITE AND THE COMBUSTION ZONES OF A BLAST FURNACE

When we consider that such eminent authorities as Sir Lowthian Bell, J. E. Johnson, Jr., and Robert Forsythe wrote their books on blast-furnace practice before the discovery and disclosure of the combustion zones in front of the tuyeres of a blast furnace, we can easily realize why some of their conclusions expressed in their authoritative books are not in accord with the more recent theories regarding the reactions taking place at the tuyere level. Clements wrote his book⁷ after the work of Perrott, Kinney, Royster and Joseph had been published, beginning in 1923. On page 450 of Clement's book is a figure showing the combustion zones, found by the men of the U.S. Bureau of Mines.

Another factor of uncertainty and much controversy is the distinction between "combustibility of coke" and the "reactivity of coke" in the combustion zones of a blast furnace. The same problem applies to the other blast-furnace fuels as well as to byproduct coke. The confusion in the minds of many blast-furnace men that arose when it was said that anthracite was more combustible than coke was because "combustibility" as used by the blast-furnace men was not explained as being something different from "reactivity" as used by the chemical-physicists. Research work by the Anthracite Institute has cleared up this problem, and the

⁷ F. Clements: Blast Furnace Practice, 1, London, 1929.

remarkable differences between coke, anthracite and charcoal have been shown in the paper presented by Keene, Turner and Scott⁸, who reported that the reacting power of anthracite was 57 per cent compared with 22 per cent for byproduct coke; and that the initial reaction temperature of the samples tested averaged 572° C. for anthracite and 715° C. for coke.

FALSE THEORIES

One of the false theories of blast-furnace practice that has persisted ever since mineral fuels were introduced, is that of "the penetration of the blast." It has shaped not only our actions and our practice, but our furnaces and our tuyeres. This false theory probably started in that single sentence of 329 words, with only commas for pauses, contained in the Letters Patent issued to Dr. G. W. Geissenhainer, Dec. 19, 1833, for his "new and useful improvement in the manufacture of Iron & Steel by the application of Anthracite coal." Dr. Geissenhainer, in his claims "did hereby declare that the mystery or only true principle and manner . . . consists in applying in an appropriate blast furnace, a blast or a column, or a stream or current of air, in or of such a quantity, velocity and density or compression as the compactness or density and the continuity of the anthracite coal, requires."

In 1898, John M. Hartman, of Philadelphia, presented a paper⁹ in which he said:

The proper penetration into the crucible of the air from the nose of the tuyere is a question not decided; but, as larger hearths are used, more penetration is required. This is of course, a function of the diameter of the nozzle. Some years ago 5" tuyeres as a maximum for anthracite, and 6" for coke furnaces were fixed by the writer, and up to date no reasons for a change have been found. A minimum velocity of 20,000 feet a minute for anthracite, and 15,000 feet for coke furnaces works well for round-nose tuyeres in crucibles up to 10 feet diameter.

At the meeting at which it was presented were some of the ablest blast-furnace men of the country, including James Gayley, Edgar Cook, John M. Hartman, B. F. Fackenthal, Jr., F. E. Bachman, Frank B. Richards and Austin Farrell—and they all believed in the "theory of the penetration of the blast."

Not until a quarter of a century later did we know the true theory of the combustion of fuel at the tuyeres of an iron blast furnace—when G. St. J. Perrott and S. P. Kinney, at the suggestion of P. H. Royster, discovered that the combustion of coke is complete 32 to 40 in. from the

⁸ W. L. Keene, H. G. Turner and G. S. Scott: Reactivity of Anthracite with Carbon Dioxide. *Trans. A.I.M.E.* (1934) 108, 303.

⁹ J. M. Hartman: Notes on Tuyeres in the Iron Blast Furnace. *Trans. A.I.M.E.* (1898) 28, 666.

nose of the tuyeres¹⁰. In subsequent tests and reports, especially in *Technical Paper 391*, U.S. Bureau of Mines¹¹, the combustion zones in front of the tuyeres were more clearly defined. One very significant statement was made by Perrott and Kinney in their 1923 paper, as follows: "Thus a given weight of blast will burn the same weight of carbon at the tuyeres, irrespective of the physical properties of the coke." This statement, I believe, has a direct bearing on the combustion of anthracite coal at the tuyeres of an iron blast furnace as well as on the combustion of charcoal at the tuyeres.

Charcoal has "only about 69 per cent of fixed carbon, or less in kiln coal¹²." A good anthracite furnace coal will have 84 to 89 per cent fixed carbon; some of the anthracite for blast-furnace fuel used when anthracite furnaces were in their prime contained as high as 94.10 per cent fixed carbon¹³. It is obvious that a ton of coke or a ton of anthracite put into the top of a blast furnace will require more cubic feet of blast for combustion at the tuyeres than a ton of charcoal put into the top of the same furnace. All the records that I have been able to compare show that coke and anthracite require about the same volume of blast per pound of fuel. My experience of Sault Ste. Marie, Ontario, was that coke took 1.44 times as much volume of blast as did charcoal in the same blast furnace¹⁴. The charcoal used in the blast furnace contained about 74 per cent of fixed carbon and about 22 per cent volatile combustible matter; some birch "body wood" contained as high as 77 per cent fixed carbon, small maple limbs would run as low as 64 per cent fixed carbon.

It would be difficult, if not impossible, to make accurate comparisons of the volume of blast required for charcoal and for anthracite, by taking the available figures of more than fifty years ago. The records are sufficiently accurate, however, for us to say that coke does not take "2½ times as much volume and pressure as does charcoal, anthracite 3½ times as much," as was stated by Dr. Geissenhainer. In the U.S. Census of 1880, Part II, Statistics of Iron and Steel Production, James M. Swank gave some data showing that the volume of blast required per pound of anthracite put into a blast furnace was 1.36 times as much as required for a pound of charcoal put into a blast furnace. When we consider that only the fixed carbon, and sometimes not all of that, reaches the tuyeres of a blast furnace, it looks as though we can safely extend the

¹⁰ G. S. Perrott and S. P. Kinney: Combustion of Coke in Blast-furnace Hearth. *Trans. A.I.M.E.* (1923) 69, 543.

¹¹ S. P. Kinney, P. H. Royster and T. L. Jóseph: Iron Blast Furnace Reactions. U.S. Bur Mines *Tech. Paper 391* (1927).

¹² J. E. Johnson, Jr.: Principles, Operation and Products of the Blast Furnace, 183. New York, 1918. McGraw-Hill Book Co.

¹³ F. Overman: A Treatise on Metallurgy, Ed. 6, 389. New York, 1873.

¹⁴ R. H. Sweetser: *Trans. A.I.M.E.* (1908) 39, 228.

statement made by Perrott and Kinney in their 1923 paper, mentioned above, to include *all* fuels and not limit it to blast-furnace coke. Their conclusion would then read as follows: "Thus a given weight of blast will burn the same weight of carbon at the tuyeres, irrespective of the physical properties of the *fuel*." I will stand by that statement until someone can positively prove the contrary.

LACK OF RESEARCH WORK IN BLAST FURNACES

If for three generations we have built and operated our blast furnaces without having had the correct theory for so important a matter as the combustion of the fuel at the tuyeres, it is likely that there are other problems of blast-furnace practice that should be solved. It is the lack of research in the iron and steel industry that has called forth such a paper as that by Mr. Ramseyer¹⁵. The suggestion of Mr. Ramseyer that the slag and iron might be removed from the hearth continuously directs attention to the fact that the hearth of the blast furnace has not yet been sufficiently explored, as far as anything published has revealed. The region of the blast furnace extending downward from the level of the center line of the tuyeres is the most important part of the furnace, yet it is the least known.

The U.S. Bureau of Mines has made some commendable attempts to work out this problem of the hearth, but it has been too much hampered by politics and lack of necessary funds to complete the big job of a thorough exploration of the hearth of a modern blast furnace while in operation. This work should be undertaken by the American Institute of Mining and Metallurgical Engineers as sponsor, in conjunction with the staff of the Bureau of Mines. The cost should be borne by the whole iron and steel industry, which is ably represented by the American Iron and Steel Institute.

CONCLUSIONS

If such a brief review of the most important "natural" blast-furnace fuel has shown that anthracite was used for over three-quarters of a century without its character being well known and its superior qualities being recognized, it then follows that possibly our present blast-furnace practice could be much improved if we better understood what takes place with byproduct coke within that big column near the center of the furnace, and what happens in the region between the level of the tuyeres and the level of the iron notch.

It would be worth while to determine whether the superior quality of anthracite pig iron was due to the anthracite alone or partly to the small diameter of the anthracite blast furnaces.

¹⁵ C. F. Ramseyer: A Chemical Engineer Views the Steel Industry. Page 159, this volume.

DISCUSSION

(C. B. Murray presiding)

W. A. HAVEN,* Cleveland, Ohio.—An understanding of the importance of gas velocity in a furnace is one thing that may lead us much further afield in the future. Mr. Boynton's paper¹⁶ very properly and capably touched upon the necessity for finding some means to reduce gas velocities through the top of the stack; however, before indicting the furnaceman for not having previously accomplished these things, it may be well to take a look at what has been done in that respect

The blast furnace used in North American practice has really been a gradual development, perhaps a development in the face of theories that we knew very little about; nevertheless, in the hands of the furnacemen who have had to guide the development, it has been wonderfully good. In proof of that, I ask you to consider the top temperature charts. Many of the northern blast furnaces today are running at 300° F. or even less of top temperature. Realizing this, you will appreciate the fact that so far as getting down in top temperatures is concerned not a great deal more could be accomplished. In some cases these temperatures are accomplished without the use of water.

Secondly, many blast furnaces today are producing fairly large tonnages of pig iron on less than 100 lb. of flue dust per ton. Thirdly, the CO:CO₂ ratios in many blast furnaces today are far below what some of the older generation of blast-furnace experts predicted could ever be accomplished. That has been reduced to as low as 1.3:1, CO to CO₂.

Those three actual facts, I believe, will demonstrate that the furnace as it has been developed, not perhaps from the standpoint of what should have been done, is nevertheless a very highly efficient mechanism. in spite of what some critics, Mr. Ramsayer among them¹⁷, contend has been a lackadaisical development.

As to the future, the blast furnace is a very large commercial instrumentality, costs millions of dollars to build, and any changes made in the construction of a furnace must recognize the fact that these millions of dollars are tied up in it. Anything that may upset the results already obtained is of no little consequence; it must be taken seriously even in such an obvious matter as decreasing the velocity of gas through the stack. It must be approached carefully. It is well known that in the South, where the ores are hard, it was found that the bell could be made much smaller in relation to the stock-line diameter. When the Bureau of Mines figures came out indicating that gas velocity could be made more uniform by distribution, some of the northern operators thought that a fine idea and took the southern practice and put it in effect on our large furnaces up here, using a small bell which would throw more of the fine ore toward the center of the furnace and more coarse materials to the walls. That was actually tried and I am sorry to say the results were so bad that they caused serious embarrassment to the operators responsible for the change.

That is certainly an obvious way of increasing the average density of the stock column, and yet in doing this it must be kept in mind that with the furnace as now designed, and with the size of the bell and stock line as now established, a certain amount of fine ore needs to be kept against the walls of the furnaces to prevent serious erosion of the walls, and if we make any radical change in that respect we may have to go back and reconsider not only the size of the stock line, but batter of the

* Vice President, Arthur G. McKee & Co.

¹⁶ Page 64, this volume.

¹⁷ Page 159, this volume.

inwall, batter of the bosh, and the size of the hearth itself. So, while it is quite easy to suggest, as has been done recently by many people, that furnacemen have been more or less negligent in taking advantage of the present status of things, I insist again it is not so.

As to the other matter of increasing the blast by using oxygen, which has been touched on repeatedly, it is not new. It is every furnaceman's dream to use gas as a fuel and undiluted oxygen as a combustion agent, but if you check up on the price of oxygen, you will find out that with oxygen at prevailing rates, it now being about 75¢ per 100 cu. ft., the procedure would use up many, many times all the savings that have been indicated by anyone that I know of.

J. N. SHERER,* Reading, Pa.—Because of my having seen great quantities of anthracite coal consumed in blast furnaces, I hope Mr. Sweetser will give some consideration to the following: The production of any blast furnace within a given time is determined by two things: the amount of fuel required per unit of iron and the amount of fuel consumed per unit of time.

Mr. Sweetser has said that the fixed carbon in good anthracite and coke is just about the same—a statement that when applied to the blast-furnace law of production, that both fuels when used separately with the same quality of iron ore, means that the same amount of fuel would be required per unit of iron.

In the books on the blast furnace by Robert Forsythe and J. E. Johnson, Jr. one comes across the statement that a unit of coke will burn from two to two and one-half times as fast as a unit of anthracite. So applying that to the second law of blast-furnace production would mean that furnaces on anthracite wholly or in part would produce a smaller amount of iron per unit of time.

In the olden days the question of proper blowing capacity and other things about the blast furnace would rather indicate they were somewhat inadequate when applied to the consumption of anthracite coal. But now with modern equipment that is sufficient for all these things, would the question of a more rapid combustion of anthracite be brought about?

Today the maximum amount of the production of a blast furnace is no longer so very fashionable and quality of the iron seems to have become the great essential.

Mr. Sweetser makes the statement that anthracite coal produces a higher quality of iron than that produced by coke. I have been wondering if in eastern blast furnaces, instead of reducing the volume of blast and slower running, the introduction of quantities of anthracite coal by slower combustion would bring about, in part, the same results.

R. H. SWEETSER.—The using of the smaller sizes of anthracite, egg size, for instance, has never, to my knowledge, been tried. I wanted to do it in 1916 but we were unable to get the size. In connection with slow blowing—as far as we know the slower combustion of anthracite brings up the question of the use of the small-sized anthracite in the modern blast furnace, and, if that could be brought about, we could get the answer to the question. I do not know of anyone who has used the egg-sized anthracite in the modern blast furnace. In the old days there were blowing engines that were just flat-valve wasters of air. When the pressure went up, the leakage was tremendous. We do not know how much it was, and that is why I said in my paper that it was impossible to compare the volumes of blast used in those old days with the volumes of gas measured accurately today, but I do believe that in the combustion of the anthracite with equipment of the right size—and that is a method, as Mr. Rich says, in which must be figured from his kinetic theory how much

* Vice President, The Thomas Iron Co.

air would be necessary to burn the carbon that is brought down to the front of the tuyere—it would take a great deal more air for the *same volume of fuel* than it does now. We do not know how much more.

In the statement that I made about the need of research, I am not now belittling what we blast-furnace men have been doing all these years, but I am bringing out the fact that we have done a great many things, designed our blast furnaces and our tuyeres, from false theories. Now that we have learned so much that takes place above the tuyeres, if we study what takes place below the tuyere level we might decide to change our designs again and we might get better results.

Some blast furnaces today are making pig iron on 1450 lb. of coke and others are using 1700 and 1800 lb., a question of importance to the steel industry, and if we would study the conditions that take place at the tuyeres and that part of the furnace below the tuyeres, we might learn a great deal more about our blast furnaces.

W. A. HAVEN.—I should like to contend also that most of the steel companies that are making 1700 and 1800 lb know why their coke consumption is higher than others, and if there is any indicting to be done, it should be more against the steel companies themselves in that they do not apply principles and equipment that have been brought to their attention to correct their operating difficulties. If they would spend a little money to do that, I think the advance would be greater and faster than it may be with further research—and I am not against research.

L. F. REINARTZ,* Middletown, Ohio.—I should like to ask Mr. Sweetser how he determined the quality of anthracite pig iron. Is it better from the quality standpoint than the pig iron we are making at the present time?

R. H. SWEETSER.—At the time that the Thomas Iron Co. was making anthracite pig iron and also making coke pig iron, tests were made at Lafayette College showing the superior qualities of anthracite pig iron measured by the tests of that time; that is, in tensile strength and in the character of the castings that were made. It was merchant iron, not steel-making iron. I do not know what the results would have been in steelmaking iron.

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Notes on the Development of the Iron Blast Furnace*

BY A. J. BOYNTON AND S. P. KINNEY, MEMBERS A.I.M.E.

(New York Meeting, February, 1935)

ABSTRACT

THIS paper states that progress in blast-furnace engineering during the past five years is unimportant except for the advent of the electric precipitator for gas cleaning. It describes improvements in certain furnace details and in materials of construction. The paper is largely given over to a discussion of difficulties in operation due to disproportion between the diameter of the present-day furnace at the bosh and at the stock line. It is proposed to remedy this disproportion, and to restore relations in the diameter of stock line and bosh as they formerly existed, by a new method of filling. This method requires a double bell arranged to discharge towards the periphery or towards the center of the furnace. Coke is classified into two sizes, the small size going to the middle of the furnace, and the larger to the periphery along with the ore. By this means the resistance of the center of the furnace is increased, and the stock line diameter may be greatly increased.

The writer believes that these modifications will result in a somewhat improved fuel economy and regularity of operation and also in a very greatly reduced production of flue dust.

* This paper will be published as A.I.M.E. *Tech. Pub.* No. 652 (*Metals Technology*, October, 1935).

Some Observations on Sponge Iron and the Properties of the Direct Steel Made from It*

BY R. S. DEAN, MEMBER A.I.M.E., E. P. BARRETT AND CALVIN PIERSON

(New York Meeting, February, 1935)

ABSTRACT

WROUGHT iron and steel have been prepared from limonite, hematite, and magnetite ores by gaseous reduction, compacting and squeezing the resulting product at high temperature and finally melting the wrought iron so formed. The structure, analyses, mechanical and magnetic properties of the products are given. It is found that the structure of iron ores is best studied by subjecting them to gaseous reduction and using metallographic technique on the resulting sponge iron. In this way the cell structure of iron ore is clearly shown. The wrought iron made by heating compacted sponge iron to 1450° C., and forging, shows a cell structure inherited from the ore. This cell structure is further preserved in melting and casting the wrought iron. The probable relation of the properties of the materials to this inherited cell structure is discussed.

* This paper was published as A.I.M.E. *Tech. Pub.* No. 592 (*Metals Technology*, January, 1935).

Ladle and Teeming Practice in the Open-hearth Department

BY G. D. TRANTER*

(New York Meeting, February, 1935)

THE importance of ladle and teeming practice and its relationship to the yield and quality of the product has focused considerable attention on this phase of open-hearth operation. Inherently bad steel cannot be perfected by manipulation during teeming, but through the proper handling of "off heats" serious losses, which in many cases arise, can be greatly minimized. Conversely, good steel can be ruined as a result of poor workmanship in the pit, and rendered unsuitable for application to orders where exacting surface and physical requirements are essential. Sufficient evidence has been secured to warrant careful investigation of pit operations when an abnormal number of basic defects develop in the semifinished product or are found on the inspection table.

This paper is written from the standpoint of the problems involved in making satisfactory ingots for sheet rolling. Furthermore, since rimming steel is almost universally used for manufacture of sheet, the data presented herein refer particularly to that type of steel.

Going back some 30 years in open-hearth history, the word "pit" properly described the hole into which the ladle was lowered to receive the metal tapped from the furnace. The working space was necessarily limited, and the disposal of slag and metal overflowing the ladle or lost because of breakouts presented a serious problem. The equipment, of course, was rather crude in the light of present-day development. Often no ladle stands were provided, the ladle being hung on the crane beneath the runner. When delayed taps occurred, the ladle was often held in position for many hours, thus tying up pit operations and causing delays to adjacent furnaces. Because of crowded conditions, slag thimbles were not used and a network of cast-steel triangles and old tapping bars, placed before the heat was tapped, was the means for removing slag from the hole. Furnaces of different capacities were used

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frequently, therefore ladles of different sizes were required, thus necessitating an auxiliary bail and hook to accomodate the various kinds.

The modern open-hearth plant, with the elevated charging floor, obviates the former unsatisfactory conditions, since the pit is on ground level with provision for more adequate working space to carry on the operations. Ladle stands beneath the furnace runner make it unnecessary to hold the crane and delay other work, and slag thimbles provide an effective means for slag disposal. Ladle cranes and runways have been designed for increased capacity and to provide a greater factor of safety. More suitable refractories have been developed, ladle equipment has been improved and there has been advancement in technique of the personnel.

Engineering and type of equipment are important factors, but even with certain limitations in this respect, a high degree of efficiency can be maintained by attention to a number of important details. In general, the factors involved in ladle and teeming practice may be summarized as follows:

1. Efficiency of the refractories.
2. Method of and workmanship in assembling the stopper rod.
3. Size of nozzle governing rate of teeming.
4. Mold design and practice.
5. Technique and manipulation in teeming.
6. Treatment and handling of ingots immediately after pouring and before delivery to soaking pits.

Running stoppers probably head the list of causes for defective product traceable to pit operations, and always involve loss of steel and safety hazards. A survey of a number of steel plants shows considerable variation with respect to the frequency of running stoppers. In some plants it is a rather infrequent occurrence while in others it constitutes a major problem. Failure of the refractories, method of assembly and drying the stopper rod are the usual causes of this very annoying difficulty. Type of steel, size of heats, number of shutoffs, and skill of the personnel also have their effect.

Diversity of opinion exists on certain details of ladle practice, but in general all plants are in agreement on certain fundamentals, which are described in the following pages. Each plant develops its particular methods to suit the needs of local conditions and to handle the type of product being made.

LADLE BRICK

Ladle brick should be sufficiently dense to prevent excessive slag penetration and have the proper constituents to resist the fusing action of the slag and metal. Physical properties are as important as chemical analysis and kiln conditions also influence results. Tight joints in the lining are essential, taking into account the necessary allowance for

expansion. By using the proper proportion of brick shapes—arch, wedge and squares—more uniform lining practice is obtained.

STOPPER-ROD ASSEMBLY

Stopper-rod assembly requires workmanship of a rather specialized nature and best results are obtained where the work is assigned to a regular stopper-rod maker who is responsible for assembling and drying rods used by all shifts.

The stopper head, usually made of graphite, is affixed to the lower end of the stopper rod by means of a bolt and key or a screw head is used. The key type of head should turn freely on the rod, but not loosely. If too tight, expansion may cause the head to split during pouring; but loose heads may burn off, if molten steel runs into the joint. A tapered bottom sleeve into which the shank of the stopper head is fitted serves as an added protection at this point.

It is also important that the key slot in the rod be accurate, otherwise a poor fit will result. The bolt hole in the stopper head is plugged with a moist compound usually obtained from the stopper-head manufacturer. Experience has shown too much variation in homemade compounds for uniform results.

Fireclay used to pack the joints between the sleeve bricks should be of flint-base clay of good quality. Experiments with various kinds of clay have shown that some grades are entirely unsuited for this purpose. A special supply of clay should be kept for use with stopper rods if that used for other purposes is not of the proper texture. Certain kinds of refractory cements now available are also very satisfactory.

A drying oven is necessary, to thoroughly dry the assembled rod before it is placed in the ladle. The vertical type is good; new rods are put in at one end and dry rods are removed at the other end. An electric monorail hoist is used for lifting the assembled rod from the bench to a vertical position, where it is attached to a trolley operating on a system of channel supports for conveyance through the furnace. The furnace is equipped with a recording pyrometer and a definite drying cycle is followed. By assembling a daily supply of rods and holding a sufficient number of rods in the furnace at all times, the drying cycle is automatically controlled. The oven has four compartments, which is especially advantageous when rods of different sizes are required. The rod must be handled carefully after removal from the oven, and it should always be held in a vertical position, to avoid cracking in the joints.

The mechanism operating the vertical movement of the stopper rod in the ladle is usually lifted to raise the rod and lowered to shut off the stream. This method has proved satisfactory from both an operating and safety standpoint. Various controversies have arisen as to the

relative merits of this method compared to that whereby the lever is lowered to open the nozzle.

NOZZLES

Nozzle setting requires careful selection of the proper mixture of fireclay and loam for ramming the nozzle into place; size and contour of the cup to properly guide the stopper head into the nozzle opening; careful drying of the surrounding clay and loam, setting the nozzle in a vertical position in relation to the mold, and examination or testing for imperfections before use.

Grinding the nozzle cup has given satisfactory results where a slight imperfection prevented a proper fit with the stopper head, but the surface must not be ground too deeply, otherwise the soft interior, beyond which the surface firing has toughened the brick, will be exposed.

Nozzle size to properly control the rate of pouring has been the subject of considerable discussion among steelmakers. Nozzle size varies with different types of steel and tons per heat but there are certain limitations in area beyond which the increased rate of pouring gives rise to interior defects in the ingot. The larger nozzle is more favorable to ingot surface, but has a detrimental effect on the interior structure from the standpoint of blowholes, pipe and inclusions.

Where many ingots are poured, necessitating frequent shutoffs, the double nozzle system has overcome much of the difficulty arising from holding the metal too long in the ladle. While the use of the double nozzle does not exactly reduce the pouring time to one-half that required with the single nozzle, nevertheless the decrease in the percentage of time required for teeming is considerable. In pouring a heat of twenty-eight 18 by 39-in. ingots with a single 2-in. nozzle, 24.53 minutes was required, whereas 19.22 minutes was required with two nozzles.

Oval nozzles have come into more general use and have special advantages where slab-shaped ingots are poured. The tendency for the metal stream to strike the mold wall on the narrow dimension has been greatly minimized. Length of nozzle is also a factor and the tendency has been toward longer nozzles. A number of plants are using nozzles 12 in. or more long. An improvement is noted with the longer nozzle, in that to a considerable extent it prevents spraying of the metal stream.

Nozzles, sleeves and stopper heads should be stored in a warm dry place and allowed to season to some extent before use. The space between the furnace regenerators serves very well for this purpose. This procedure is particularly advantageous in cold weather to avoid spawling or cracking when the assembled rod is placed in the drying oven.

LADLE DESIGN

Ladle design has been given considerable thought and attention with the increased capacity of open-hearth furnaces. In many cases

existing furnaces have been rebuilt for tapping larger heats and certain limitations with respect to size, weight and design of ladles have had to be overcome.

The effect of ferrostatic pressure must be taken into account, and this is largely a function of the size and design of the ladle. A deep ladle increases the pressure but a smaller area of the metal surface is exposed to the slag during the teeming operation; a shallow ladle causes less "head" to the metal, but a greater surface of the metal comes in contact with the slag. Either extreme should be avoided by arriving at the proper ratio of height to diameter.

Oval ladles have been a solution where increased depth would be detrimental to quality or where clearance and limitations of certain existing equipment would be a problem. Welded ladles have made it possible to increase the size of heats where building columns, crane runways and ladle cranes had not sufficient capacity to carry larger heats. The welded ladle is approximately 25 per cent lighter than other types of the same capacity.

The practice of insulating ladles, which has been successfully accomplished, lowers radiation loss through the shell of the ladle. The insulation consists of approximately 1 to $1\frac{1}{2}$ in. of insulating cement applied with a trowel to the inside of the tank. This practice had for its original objective the use of a thinner lining, to increase the capacity of the ladle. The calculated radiation loss of the thinner lining without insulation indicated too much heat transfer, therefore the use of an insulating material was given a trial. After considerable experimentation a satisfactory insulating cement was found which served the purpose very well. While no actual heat-conductivity calculations have been made, the outside of the ladle indicates only a slight increase in temperature to the touch. The thinner lining has been entirely satisfactory and no decrease in service has been noted.

Various kinds of fuel have been used for drying and heating ladles—coke baskets, small slag pots, wood fires, natural gas, and fuel oil, among others. Effective application of heat for drying ladles, nozzles and rods is a very important feature of good ladle practice.

MOLDS

Mold practice has considerable bearing on the life and service of the mold, together with the surface qualities of the ingot. The use of larger ingots has increased mold problems to no small extent, particularly of the slab type, in which the large flat area is very susceptible to fire cracks and gouges.

Design is important and the mold manufacturer is directing considerable attention to this phase of the subject. Wall thickness, inside

taper, and radius of the corners are among the features being studied. Chemical analyses, physical condition of the iron, and mold-casting practice are also important factors.

Relation of mold weight to ingot weight is taking on more importance, and considerable variation is found in comparison of different plants. The structure of ingots poured into sand molds has been found to consist almost entirely of columnar crystals, therefore the rate of heat transfer of the thin-walled mold versus the heavy-walled mold should be given consideration from this standpoint.

Greater importance is being attached to mold cleaning and its effect on quality and mold life. Inclusions, surface defects and mold stickers result from poorly cleaned molds. Often a haphazard job results when the mold yard gang is required to stand on top of the mold to perform the operation; the amount of cleaning in this case being more or less in proportion to the temperature of the drag. This condition is further complicated by a serious safety hazard.

A more effective job of cleaning is done when molds are placed on the ground. Where certain limitations of equipment would necessitate too much time for this method, provision can be made for overhead cleaning whereby a satisfactory job can be made. A movable platform operating over the train of molds provides a safe and effective means for cleaning. Fewer men are required because of less fatigue due to heat, and safety hazards are practically eliminated. Slag, oxides and other foreign material are carefully scraped from the mold surface, after which the mold is hoisted and the stool scraped and blown off with compressed air.

Various mold coatings are used, with graphite or tar predominating. Graphite is applied with a spray and the mold surface is brushed after application, to prevent dripping down the side. Molds are coated with tar, either by spraying the inside surface or dipping the entire mold into a tar bath.

A pouring cycle of approximately 8 to 10-hr. intervals is usually established to avoid pouring into hot molds or molds that are too cold. A temperature best described as "hand warm" will give most satisfactory results.

Mold failure, assuming that the mold is properly designed and cast, results from a number of causes. Grade and temperature of steel poured, time allowed for it to remain in the molds before stripping, and mechanical abuse are among the principal factors affecting mold life.

Deeply gouged stools are detrimental to mold life and definite rules should be established as to the depth of gouge at which the stool is taken out of service. Furthermore, the metal adhering to the butt of the ingot, patterned by the gouge in the stool, is a total loss to blooming-mill yield. Obviously the proper economical balance must be maintained between yield, mold and stool life.

A mild-steel plate of 14 to 16 gage placed on the stool before teeming decreases the wear caused by the stream when the nozzle is first opened. The fit between the bottom of the mold and the stool is also important, to avoid excessive erosion of the bottom of the mold and large fins on the ingot.

Copper stools have been used to some extent to increase the life of both the mold and stool. Experiments indicate that less gouging of the lower part of the mold occurs when used in conjunction with a copper stool. The longer life of the stool overcomes the tendency for stools to cut away, thus making a better fit with the bottom of the mold. Experiments along this line are being observed with considerable interest.

Where ingots, because of limitations of stripping equipment, must remain in the molds for a long period of time, fire-cracking of the mold surface and gouges result. Where such conditions exist, consideration should be given to providing the necessary equipment so that molds may be promptly removed from the ingot. The use of an extra drag of stripper buggies may be used as an expedient in some cases. Mold life is materially decreased where ingots are not stripped promptly.

Ingot defects arising from defective mold surface such as fire cracks and gouges cause varying degrees of surface trouble in rolling. In most cases, light gouges and fire cracks are removed by soaking pit heating. If fire-cracked too deeply the pattern cast on the ingot tends to lap over during rolling, causing slivers and scabs. A defect resembling rolled-in scale may also result from the same condition. Badly gouged molds are the source of scabby bars, particularly where the gouge is heavy at the bottom; especially when ingots are rolled butt first.

TEEMING AND ITS EFFECT ON SURFACE

Scabs resulting from stopper troubles are usually readily identified; they vary from the size of a small coin to large patches covering a considerable portion of the bar. No reasonable amount of washing of such ingots in the soaking pits will clean up the surface.

The effect of running stoppers on the bar surface is variable. Often a full running stopper has caused less surface trouble than merely a leaky stopper. Very scabby bars result from the latter because patches or scabs freeze to the ingot surface but do not weld tightly to the surrounding metal. A full running stopper, however, causes interior defects which in many cases render the steel unfit from the standpoint of laminations and inclusions.

"Cold heats" are also causes of scabby bars and certain forms of interior defects. Usually they are primarily due to open-hearth furnace conditions and are not the responsibility of the ladle crew. Scabs often result from improper pouring technique. Where the stream is allowed

to strike the mold wall, poured too slowly or splashed because the nozzle is opened too suddenly, similar surface conditions occur.

Good teeming practice is to open the nozzle slowly until a pool of metal several inches deep has formed in the bottom of the mold. This pool of metal serves as a cushion, and prevents a certain amount of splash when the nozzle is opened to a full stream. When the ingot is teemed to approximately two-thirds to three-fourths the desired length, the stream should again be reduced and poured rather slowly until the mold is filled. This serves to "top off" the ingot, creating less splash, and allows a certain amount of gas to be evolved. The degree of splash, beyond that normally controlled through the use of the proper size of nozzle or by the steel pourer through manipulation, obviously is an engineering problem, since it is a function of the size of heat, ladle dimension and height of mold.

Splash scabs of varying degrees are formed on the ingot surface, due to conditions during pouring, and in most cases are scaled off in soaking-pit heating. However, when ingots tend to have subcutaneous blowholes close to the surface, heavy scaling is decidedly detrimental from the standpoint of seams and other defects originating with "thin-skinned" ingots. Experiments with the use of various mechanical methods for preventing splash scabs have been made with rather indifferent results. Inserts made of various materials placed in the lower part of the mold, pouring through hollow pipes, and the use of tun dishes, have failed to make sufficient improvement in the final product to compensate for the added expense. Safety hazards, and sometimes even worse surface conditions, were the net result of the experiments. "Thin-skinned" ingots also cause certain types of surface defects. In most instances such ingots are primarily due to pouring temperatures and deoxidation practice and do not originate in teeming operation. They are a very dangerous form of defect and give rise to seams, scabs and rolled-in scale on the bar surface.

In the manufacture of rimming steels, overdeoxidation must be carefully avoided. To prevent riser heats, which often are the result of overdeoxidation, it is the usual practice to slightly underdeoxidize in the ladle and complete the treatment in the molds. Observations on the pouring platform often disclose considerable variation in the practice of adding aluminum to ingots. Both the method of adding and the quantity used have considerable bearing on the quality of the product. Large additions of aluminum to the ingot are not advocated and best results are obtained where the ladle addition is sufficient to deoxidize the metal to the point where only a limited amount is required in the molds.

CAPPING INGOTS AND PULLING HEATS

Before placing the cap on the ingot, it is beneficial to remove the slag or skum that is formed during the effervescing action in the molds. This

material can be blown off with compressed air or removed by scraping with a wooden pole or paddle. This practice serves to prevent ingots from "blowing up" or spouting, a quality and safety hazard which otherwise frequently occurs where large slab ingots are poured. Considerably more slag and scum is formed on the top of ingots worked in this manner, indicating possibly that more gas and inclusions are expelled before solidification.

Pulling heats too quickly after teeming has considerable bearing on the formation of interior defects. Repeated experiments have demonstrated that certain types of laminations result from moving the ingot too quickly after pouring, and charging into the soaking pit too rapidly. The possible delay in holding the heat 15 or 20 min. is more than compensated for by improved quality results.

TECHNIQUE

Maximum results are obtained where the organization receives constant and intensive training in standard methods and practice. Technical literature, in the main, has dealt with the personal equation in a more or less abstract manner. The human element is a very important factor affecting ultimate results. With even the best of equipment, efficiency is largely dependent upon the knowledge and technique of the personnel.

To be effective, the training program must be practical and deal with specific items of practice and subsequent results. Group conferences, individual instruction by the foreman, together with frequent review and explanation of standard practice methods will materially assist in developing a highly trained personnel. The training program should incorporate the safety features of the work as well as technique and operating practice. No operation in the steel plant presents more potential safety hazards than the open-hearth pit. Safe and efficient handling of molten metal and slag requires not only safe practice on the part of the individual but also continual and special attention to the equipment.

Ladle trunnions should be inspected frequently for defects and flaws, which may develop as a result of overflowing slag. Crane runways should be regularly checked for loose rivets and worn rails. Regular inspection of ladle cranes covering mechanical, electrical and safety features is important. The inspection is more rigid where the inspection committee consists of persons who do not have direct supervision of these particular cranes. Hoist cables should be arbitrarily renewed, based on total tonnage handled over a period of time. This varies from 300,000 to 400,000 gross tons, depending on the size of cables and general conditions to which they are subjected.

Handling of oxygen equipment on the pouring platform presents safety hazards, which can only be overcome by careful regulation of

pressures, keeping oxygen hose in good condition, and proper use of the blowpipe or lance. Wherever possible a central oxygen station piped to the various points of use will reduce waste and safety hazards to the minimum. Welded joints in the piping system are recommended.

Protective apparel such as leggings, jackets and goggles should be provided, and very definite and rigid rules established for their use. It is a paying proposition from the standpoint of personal safety and more effective handling of bad heats to provide the men with the necessary protection to cope with such emergencies.

Order and clean-up in the pit is fundamental to good workmanship as well as safety requirements. Quality of work reflects the general working conditions surrounding the job. Where skulls and pit scrap are cleaned up and shipped out daily, attention is more quickly focused on excessive scrap losses at the time of occurrence.

CONCLUSION

The emphasis that has been placed on ladle and teeming practice in the foregoing should not be construed to infer that all the ills of the steel business can be saddled on this particular phase of plant operation. Soaking-pit heating and subsequent rolling have an important bearing on the degree to which inherent defects are developed.

Through proper cooperation and working arrangement between the open-hearth and blooming-mill departments, the effect of certain types of defects originating in the ingot can be greatly minimized. When the mill receives prompt notification of certain characteristics with respect to the behavior of the metal during teeming, added precautions may be taken and special treatment given in heating and rolling. The practical application of this plan whereby the two departments are brought into closer relationship has been very successful.

DISCUSSION

(Earl C. Smith presiding)

R. C. Good,* Pittsburgh, Pa.—It is common practice to tell the steel pourer to open slowly and then open up fast after he gets a pool of metal, but he has to do that with a simple lever. If we apply the principle of the movement of a hand on a clock and imagine the vertical link connected with the end of this arm, and have a bellcrank for a lever, we have a movement that gives a relative motion of the vertical pin as it moves around the clock. We cannot use that as it stands, because it is limited at the close, and we may want to move the stopper down farther as we pour steel, but we can use that principle of the bellcrank connected by links to the vertical part of the pouring or the stopping mechanism. We machine a slot in this bellcrank in which a pin connected with the lower end of this vertical part can slide at will but controlled further by a slotted stationary slide that regulates the vertical movement of the stopper. I have not figured out the angles but I have thought that with

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such an arrangement the steel pourer would move his lever through a distance of a foot or 18 in., and give a vertical movement of a fraction of an inch according to the length of the slot, and in movement of the lever through a foot or 18 in. the pin would enter the bottom of the vertical slot and there would be a nice, wide opening.

W. E. BUCK, * Granite City, Ill.—One type of stopper that has won a great deal of favor in our part of the country was not mentioned by Mr. Tranter—the bayonet type. The stopper is put on the end of the rod and given a twist of about a third of a revolution, and it tightens itself. It has been used by a number of steel foundries and in our own plant.

* Metallurgist, Granite City Steel Co.

Insulation and Control of Open-hearth Furnaces

By WILLIAM C. BUELL, JR.*

(New York Meeting, February, 1935)

As used in connection with open-hearth or other high-temperature operations, "insulation" refers to a multitude of substances, natural or manufactured, that have the one principal property of preventing the flow of heat by conduction to a greater degree than refractories can prevent it, the principal properties of the latter being resistance to temperature and/or chemical action.

The term "control" as commonly applied to the mechanization of management functions is inappropriate without qualification, for without some degree of control of every operation we could produce no steel worthy of the name.

Although grouped together in this paper, insulation and control in open-hearth furnaces have little, if any, interrelationship, therefore the paper is made up of two distinct parts.

INSULATION OF OPEN-HEARTH FURNACES

More than ten years ago the writer proposed the insulation of an acid open-hearth furnace system below the charging floor, and it was accomplished, with gratifying results. Possibly that was the first time the insulation of regenerators and slag pockets of any open-hearth furnace was undertaken, but shortly thereafter such insulation became general, and when the six groups of 150-ton furnaces¹ were built in 1929-1930, they were completely insulated below the charging floor.

While the practice was accepted at least five years ago, it was not well understood, however, as indicated by the following incident which occurred in connection with an installation made in 1929. After the

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¹ The groups are as follows: (1) 14 furnaces, Illinois Steel Co., South Chicago, Ill.; (2) 7 furnaces, Illinois Steel Co., Gary, Ind.; (3) 3 furnaces, Youngstown Sheet & Tube Co., Indiana Harbor, Ind.; (4) 6 furnaces, Great Lakes Steel Co., Detroit, Mich.; (5) 6 furnaces, Bethlehem Steel Co., Sparrows Point, Md.; (6) 6 furnaces, Bethlehem Steel Co., Lackawanna, N. Y.

plant had been operating for some time, a technical executive of the company found that the cooler side of the refractory brick of the regenerator, which, of course, was in contact with the insulation, was at a low red temperature, possibly at 1100° or 1200° F., which so startled him that he at once ordered the removal of all insulation on the roofs of the regenerators and fantails, and much argument was required to convince him that the condition was a normal manifestation of effective insulation.

In view of the present general acceptance of insulation below the charging floor, the discussion herein will be confined to the subject of the insulation of furnaces above the charging floor, for at present that subject is of very general interest, and the many arguments regarding this practice indicate a considerable difference of opinion concerning the alleged benefits of the practice.

While it is almost impossible to satisfactorily insulate the upper furnace of many if not all of the open-hearth furnaces built prior to 1929, this offers no reasonable or logical basis for argument against the advantages of insulation applied under proper conditions. It is unreasonable to expect to convert model 1910 or 1920, or even 1925, into 1935 models through the addition of one or two simple, extraneous improvements.

The insulation of the upper furnace will be only partially effective or advantageous unless the furnace and its system are fundamentally of correct design to accommodate such an improvement and the operations practice is appropriately modified; and until these facts are recognized there will be a continuance of the failures that at the present time are severely militating against the general and rapid adoption of this valuable improvement.

The question may arise: "What are the improvements in the later furnaces that cause them to take the insulation of the upper furnace with so much better effect?" The furnaces built in 1929-1930 have much higher roofs, much longer throats and downtakes, with more ample proportions of the auxiliaries below the floor, all of which lead to a freer working system, having a marked reduction of the several critical locations, which in cramped furnace design cause much maintenance trouble and short campaigns.

A few figures of furnace length (over-all brickwork) will be enlightening in this connection. Furnaces of older models of large rated tonnage, all from different plants, show: a 300-ton furnace, 79 ft. 0 in.; two 200-ton furnaces, each 68 ft. 6 in.; a 150-ton furnace, 70 ft. 0 in. From five plants containing furnaces of the more modern group: a 135-ton unit, 77 ft. 6 in., and the 150-ton designs, 78 ft. 0 in., 83 ft. 0 in., 84 ft. 0 in., and 86 ft. 3 in. Thus, the older furnaces, having nominal capacities up to double those of the newer, are from 8 ft. 0 in. to 16 ft. 3 in. shorter in over-all length than the later group, which is most significant, especially where insulation is discussed, for it indicates an abridgment of end

design which in itself magnifies temperature and erosive action on the primary refractories. The application of insulation to short-life areas is always disastrous.

SCHEDULE OF CLASSIFICATION OF INSULATING MATERIALS

Many substances of various physical characteristics are offered for the insulation of the upper furnace, none of which are suitable for general application. In order to simplify the specification and the appropriate application of the several materials, the writer has adopted five arbitrary classifications of insulating material that have been found most convenient in any consideration of the subject, which are included in abstract form herewith.

Class A Insulation (Hard Brick).—This class comprises a group of materials of which the chief characteristic is ability to maintain their original volume and shape at 2000° F. or more under loadings of considerable magnitude. They might properly be termed “semi-refractories.” Although their relative resistances to heat flow are not great, their structural features make them indispensable. This class of insulation should be used immediately under buckstays, in back walls, and in the side and ends of the bottom pan. These materials are fairly costly and their use should be confined to locations where their structural properties are required.

Representative of this class are B. & W. 80, Sil-o-cel super brick, C-22 brick, Armstrong, 111 and 444 brick.

Class B Insulation (Soft Brick).—This class includes a number of materials having the highest heat-retarding properties of the commercial insulators. They have little crushing strength and consequently should not be used under other than nominal superimposed loadings. Excessive shrinkage or disintegration may be expected if they are subjected to temperatures much higher than 1500° F. They are most useful for application in side walls where plating or grating is used and over areas where furnace-gas temperatures will not exceed 2500° F., which in open-hearth practice will be below the charging floor.

Non-pareil, Sil-o-cel (natural), Superex, and Alumino Hi-temp are representative of this classification.

Class C Insulation (Loose Materials).—There would appear to be many materials available in powdered, granular or wool form that have desirable characteristics as insulation when correctly used, and which might be listed under this classification. Such materials are of zero compression value and in several instances are effective as insulators only as long as they remain in a fluffy condition. These materials are used on roofs and plated vertical walls. While there are exceptions, fusion, disintegration or shrinkage is common when these materials are heated higher than 1600° F.

The following materials would be included under this classification: Sil-o-cel powder, granular C-3, expanded vermiculite, mineral, lead and blast-furnace slag wool, et cetera.

Class D Insulation (Cements or Plasters).—This is class C insulation when mixed with a binder such as asbestos fiber and/or a bonding substance such as portland cement, and dampened and troweled on roofs or unplated vertical surfaces. The use of plasters is not a particularly satisfactory method of insulating vertical surfaces, although often used.

Class E Insulation (Insulating Concrete).—While having only slight value as insulating material, insulating concrete will support any dead weight loading found in furnace refractories, when the interface temperature of the material is as great as 1600° F. This is the material generally employed for insulating the pan containing the furnace hearth. It finds general application for the insulation of subgrade vertical walls, and for the protection of refractory-covered areas of foundations. The best known material of this classification probably is C-3 concrete.

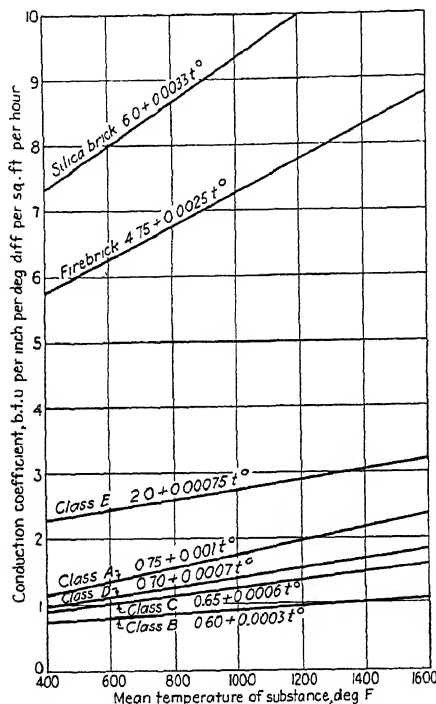


FIG. 1.—CONDUCTION COEFFICIENTS.

classifications (A, C or D and E) are necessary for the correct insulation of the upper furnace, and a like number (A, B or D and E) for the system below the charging floor. The conducting qualities of the several classes of materials as well as those of firebrick and silica brick are given for comparison in Fig. 1. The empirical conduction equations shown and used as the bases of the chart lines are convenient to use and accurate enough for any technical purpose.

Causes of Failure.—Failure of insulated furnace components may be charged invariably to excessive temperature effects created by the improper application of insulating materials. Probably the most common failure is caused from the heating of a portion of the silica brick beyond the softening point, with an ensuing distortion of the hotter portion of the brick so as to allow direct flame action on the sides as well

Requirements for Correct Insulation.—This schedule indicates that insulation of three

as the normally exposed end. The rate of failure of any refractory is enormously increased by heating on more than one surface.

Another cause of failure develops from the fusing of insulating material that has become unduly heated, thus developing chemical effects that soften or otherwise weaken the silica brick.

The duplication of such failures leads to the conclusion that the common temperature effects within the body of masonry resulting from the application of insulation are not well understood and that the lack of this knowledge is severely hampering the forward progress of economical steelmaking.

SOLUTION OF HEAT-FLOW PROBLEMS

The measure of any masonry structure to the flow of heat is its combined thermal resistance R , which is the sum of r_1 , r_2 , r_3 , etc., the individual thermal resistances of the several different materials that may make up the refractory structure. For instance, in a bare silica roof there will be but a single r , while in a back wall containing ground magnesite, chrome, firebrick and insulating brick, there will be four.

In the denominator of the common heat-flow equations there may be several terms such as $\frac{x_1}{c_1} + \frac{x_2}{c_2} + \dots$ etc. In these, x is the thickness of a particular material as used, in inches, and c is the coefficient of heat transmission (conduction) B.t.u. per sq. ft. per in. thickness per degree differential temperature per hour, and $r_1 = \frac{x_1}{c_1}$ when solved.

If the temperatures of the hotter refractory surface and the surrounding air are known or assumed (2900° and 100° F. respectively, in the ensuing discussion) the flow or emission of heat through the masonry will be a function of the combined resistance R . This relation may be seen in the equation:

$$\text{Temperature of hotter surface} - \text{temperature of cooler surface} \div \text{thermal resistance} = \text{emission, B.t.u. per unit.}$$

However, the cooler surface temperatures and the interface temperatures of the refractories alter greatly with changes in R .

An abstract of the chart used by the writer in the solution of roof problems is shown in Fig. 2 and two sets of conditions are distinctively shaded. In this 12 in. is assumed to be the minimum and 18 in. the probable maximum thickness of silica brick that will be used in roofs.

Under the conditions surrounding uninsulated roof practice, R will be about 1.0 for 12-in. silica-brick thickness, and 1.6 for 18-in. thickness. Using the chart as indicated thereon, at $R = 1.0$ and 1.6, respectively, the cooler surfaces will be 575° and 475°, and the emission, 2300 and 1540 B.t.u., respectively.

If it is now assumed that the roofs are insulated to develop $R = 3.5$ or 4.0 , the contingent conditions will change greatly to show cooler surface temperatures in the order of 315° and 295° respectively, with emission at 750 and 630 B.t.u. Thus, increasing the thermal resistance R of the roof from 1.0 or 1.6 to 3.5 or 4.0 by the addition of insulation saves from one-half to two-thirds of the heat radiated from the bare roofs.

The foregoing may well be termed the quantitative solution of an insulation problem, but this is only one part, and possibly the least important part of the problem. The second and perhaps more important part will be the qualitative analysis, in which the interior refractory

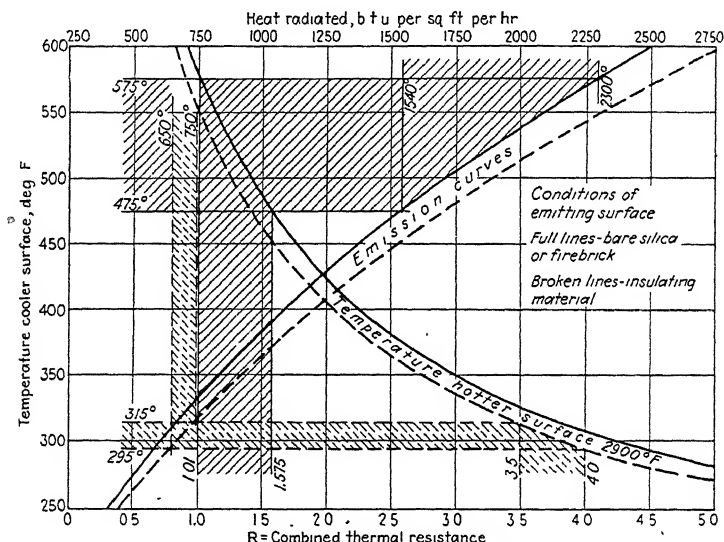


FIG. 2.—HEAT-FLOW RELATIONS.

temperatures are developed. The qualitative calculation is easily made by the following procedure:

In the problem of the 12-in. bare roof the temperature of the hotter surface has been assumed at 2900° and the temperature of the cooler surface found as a function of $R(1.01)$ to be 575° and the emission 2300 unit B.t.u., and thus all the germane data are assembled.

If insulation is added to the roof to increase the R to 3.5 , then, as above, the hotter surface temperature is assumed as 2900° , the cooler surface temperature found through the use of the chart as 315° and the emission 750 unit B.t.u. The data on the insulated roof are now complete, except those with reference to the temperature at the interfaces of the two materials. Owing to its higher average temperature, r_1 of the 12 in. of silica brick drops to 0.842 , and consequently r_2 for the insulating material necessary to develop $R = 3.5$ will be $3.5 - 0.842$, or 2.658° .

The temperature drop through the silica brick may be found as the emission $(750) \times r_1(0.842)$, or 622° , which deducted from 2900° gives the interface temperature at the junction of the silica brick and insulation of 2278° .

Two series of roof refractory arrangements are shown in Fig. 3, one including 12 in. and the other 18 in. of silica brick, each series starting with bare silica roofs which are progressively insulated to develop $R = 4.0$. It is interesting to note the considerable reduction of the thermal resistance of the silica brick by the addition of insulation, a condition generally overlooked.

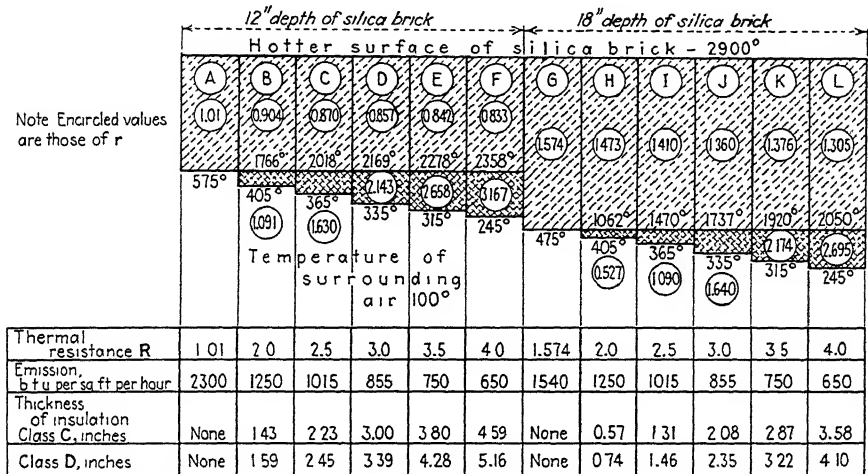


FIG. 3.—COMPARATIVE THERMAL EFFECTS WHEN 12-IN. AND 18-IN. SILICA WALLS OR ROOFS ARE INSULATED TO VARYING DEGREES.

It is evident that all of the insulated items of the 12-in. series except *B* and possibly *C* show temperatures at the junction of the silica brick and insulating material that are too high for safe use. The table at the bottom of Fig. 3 shows that less than $1\frac{1}{2}$ in. of class C and a trifle more of class D insulating material are required to raise the thermal resistance of item *B* to $R = 2.0$. Such a thin coating of insulation is seldom proposed.

As a 12-in. silica brick may be expected to decrease 25 to 40 per cent in thickness during a campaign, and probably will have a lessened proportional thermal resistance, a coating of insulation suitable for use with full-depth brick will cause excessive and probably destructive temperature effects. Supported by several experiences, the foregoing study leads to the definite conclusion that a 12-in. silica open-hearth roof should not be insulated.

As long as the roof brick are at full depth it appears that the 18-in. series could safely be insulated to $R = 3.5$ and even possibly to $R = 4.0$. Towards the end of a campaign the 18-in. original silica depth will be

reduced to 12 in., or even less, but assuming 12 in. it is possible to approximate the condition of the original 18-in. roof by reference to the items of the 12-in. series carrying a similar depth of insulation.

Thus original item *K*, $R = 3.5$, towards the close of the campaign will approximate item *D*, which develops excessive interior temperatures, or original item *J*, $R = 3.0$, will later approach item *C*, $R = 2.5$, with dangerous interior temperatures for a roof weakened by erosion, and item *I*, $R = 2.5$, may later be similar to item *B*, $R = 2.0$, in which all temperatures are nominal.

SAFE AND UNSAFE INSULATION

From the foregoing the conclusion may be drawn that the 18-in. silica roof may be safely insulated and no adverse effects encountered through the campaign if the original thermal resistance of the series refractory is placed at about $R = 2.5$.

Silica roofs having the intermediate thicknesses of $13\frac{1}{2}$, 15 and 16 in. are frequently found in use in the practice. A continuation of the studies by methods parallel to those described show that the $13\frac{1}{2}$ -in. roof should not be insulated. The insulation of the roofs of the other thicknesses may be found advantageous if carefully conceived and executed.

IMPORTANT CONSIDERATIONS

Fig. 3 indicates also a number of vital points that deserve thorough examination. The first is that the savings of radiated heat often cited as the chief advantage of the application of insulation must be subordinated to the data of interior temperature effects. The second, that the thermal properties of a given insulating material must be well understood and the material applied accordingly. The third, that the use of too great a depth of insulation will unquestionably lead to severe troubles during the campaign. The fourth, that it is best to under-insulate slightly. And finally, that nothing in connection with the application of insulation should be left to the imagination of the masons.

The practice of taking the temperature of the roof brick under the insulation on recording pyrometers, and instructing the first helper not to allow a stated temperature to be exceeded, a practice that has been applied to several units, may lead to operating difficulties unless constantly increasing temperatures are established for the thermocouple contact as the campaign progresses. If the roof item *I*, Fig. 3, is equipped with such a pyrometer, the appropriate thermocouple temperature when first operated would be perhaps 1500° but towards the end of the campaign might exceed 1800° . The continued requirement for 1500° probably would appreciably reduce production.

While a considerable saving of fuel may accrue from the correct use of insulation, a great advantage may be found from a saving in the refractory

upkeep costs if the insulated furnace is fundamentally correct in its design, and the insulation understandingly applied.

Mineralogically, silica brick, when it is first placed in position in the furnace, consists largely of quartzite. When elevated to temperatures 800° to 1400° F., it undergoes two and possibly more petrographic changes, and, except as a result of long-continued heating, reverts to its original quartzite form when cooling. It is within the temperature range of these form changes that cleavage and spawling occur as a result of expansion differences.

Both of the uninsulated roof bricks, items *A* and *G*, Fig. 3, show hotter surface temperatures that are above and cooler surface temperatures that are below the critical range. From this it is evident that at some points within the brick these changes of form must be continually going forward and backward with any material variation in furnace temperature, such as occurs several times daily, and the bricks are severely weakened structurally as a result.

In all of the insulated arrangements, excepting perhaps item *H*, both the hotter and cooler surfaces of the silica brick are well above the critical range, consequently the frequent petrographic changes, ever present in the bare roofs, are absent, and the life of the insulated components thus substantially lengthened, and as roof life is usually the governing factor of campaign length, a greater ingot tonnage is secured on a rebuild, with a proportionate decrease in the rebuilding cost.

CONTROL OF OPEN-HEARTH FURNACES

The control of open-hearth furnace is the entire management of a unit, including the metallurgical procedure, and is the responsibility of the melter, who delegates to the first helper certain control factors. The control of a furnace includes the two covering functions of the operation; namely, the control of the fuel incoming and of the furnace gases outgoing. Seven important items are included in these functions, as follows:

Control of Incoming Fuel

1. Control of temperature.
2. Control of flame direction.
3. Control of flame development.
4. Control of fuel quantity.
5. Control of combustion quality.

Control of Outgoing Furnace Gases

6. Control of pressure in furnace laboratory.
7. Control of regenerator temperature.

The following analysis is made to show the factors that necessitate their control or adjustment, and to what extent instrumentation may correctly react to develop the condition sought:

Control of Temperature.—Temperature qualitatively or heat quantitatively must be varied at several periods of the operation, and if not

accomplished rapidly when necessary may lead to serious difficulty or damage to charge or furnace. Probably this is the most important management factor of operation. While in most cases a change of the fuel rate is the method of modifying temperature, the bath temperature is often deliberately altered through the use of certain metallic additions. There is no instrument that will indicate all of the several conditions of temperature and heat that must be constantly observed and considered, and until such an instrument is available the mental and ocular reactions of the first helper must be depended upon to cause the desired condition to be developed and maintained.

Control of Flame Direction.—The control of flame direction is a prime factor in tonnage rate and upkeep cost. Unfortunately, little if any control of direction is possible during a heat, with furnaces of the producer-type, but a considerable exercise of control should be possible with the end firing of fixed fuel. Properly practiced, flame directional control develops several real advantages but, as with item 1, the results attained are entirely dependent on the first helper's reactions and actions. No instrumental control of this factor has been proposed.

Control of Flame Development.—The control of flame development is as the factors of the two preceding items, a matter of importance that may be managed only through the ability and care of the first helper. At several periods of the operation a long, soft flame is best; at other times a shorter, sharper flame will do faster work, and various intermediate flame effects are desirable at other times. Manipulation of various devices of operation are necessary to accomplishment of appropriate adjustments in this respect.

Control of Fuel Quantity.—This is merely a means to an end to accomplish the temperature control. As it has been shown under item 1 that temperature and heat input cannot be measured with sufficient accuracy to assure the success of the process should the process be carried on from such an indication, and as such an indication must furnish the motivating impulse if fuel quantity is to be instrumentally controlled, it is obvious that the control of fuel flow must continue to be a manual function.

Control of Combustion Quality.—The control of the combustion quality is an important item in economical furnace operation. The best quality of the flame at any time would be a flame or the resulting combustion gases of a chemical composition with correct physical characteristic that would most aptly conclude a desired effect. Actually, the most economical furnace operation will be secured if combustion quality is varied several times during the steelmaking operation. Various devices are offered for the instrumental control of combustion quality, on the premise that a combustion quality approaching the theoretically perfect, maintained constant throughout the heat, is the superior condition.

this premise is faulty and even though most of the devices may be regulated or altered to the gas composition desired, their use, instead of developing any particular advantages, thus far has sometimes developed counter effects.

Control of Pressure in Furnace Laboratory.—Among the operating factors, the control of furnace pressure ranks next in importance to the proper adjustment of temperature and heat, for furnace pressure has much to do with fuel and tonnage rate as well as refractory life and cost. As fuel and air enter the furnace under a positive pressure head, and the outgoing furnace gases flow through the downtakes under the influence of negative pressure effects, it is obvious that at some point between entry and exit a balanced draft—neither pressure nor suction—must be effected. Pressure conditions within the furnace are constantly changing both as to location and intensity and are subject to modification by dynamic and static as well as chemical and thermal effects. They are also generally affected as to location by furnace reversals. The positive pressures encountered in the furnace laboratory are minute, other than momentarily, seldom exceeding 0.005 in. water column. At this measurement the “sting-out” at a wicket opening will be so considerable as to indicate at once the necessity for reducing the furnace pressure. Minus pressures of considerably greater intensity may be developed without outward indication. The ideal pressure condition in a furnace laboratory would most likely be a completely balanced draft over the entire bath, which would effectively prevent the outflow of heated furnace gases or the inflow of cold atmospheric air. As this is impossible of accomplishment, the most satisfactory compromise is found by experience. Furnace pressure conditions are managed by appropriately controlling the waste gas flow in the effluent system.

Control of Regenerator Temperature.—The control of a regenerator temperature through thermocouple indications is a recent improvement. Correctly installed, this is proving a valuable aid to operation in that a greater preheat temperature may be secured and the liability of damaging the checkers by overheating minimized. In the considerable interval between the very early stages of the heat and the latter part of the finishing operation, temperature indications from the regenerative system are the most satisfactory means of establishing reversal time.

Of the seven items listed above as factors of operation, all, with the exception of the adjustment of flame, item 2, are controlled by opening, closing or manipulating valves, therefore any or all of these six items may be instrumentally controlled if an appropriate impulse emanating from an appropriate point may be transmitted to the operating mechanism, causing the operating means to react appropriately. The development of sufficient power to move the heavy, cumbersome valves and other operating media of the open-hearth furnace through the tiny indication

of delicate antennae placed at the point of indication is the base upon which the principal operating aids are developed.

METHODS OF CONTROL

I. MANUAL CONTROL.

1. The original method of control, entirely mental or ocular and without instrumental aid or motivated means for accomplishing the physical actuation of the control apparatus.
2. Motivated control apparatus, relieving the operator of all but nominal physical exertion in furnace management.
3. Simple instruments through the use of which certain conditions may be better understood, duplicated and sustained.

II. INSTRUMENTAL CONTROL.

1. The individual mechanized control of one or more of the functions of operation through the use of which the function or functions are stabilized in a desired condition and maintained thereat without further attention of the operator.
2. The individual mechanized control of all of the functions of operation and in addition interlocking and interconnecting their relations so that the entire operation or continuity is accomplished without further attention of the operator; in other words, automatic control.

All ingot producers take pride in the belief that they are progressive, but as a matter of fact the elementary methods specified under I-1 are still often observed on the control platform and valve bay of many open-hearth plants. While the reversing of the furnace valve system is universally accomplished by other than manual means, it is usual to find that all adjustments of the heavy valves must be made manually, and because of the physical effort required desirable adjustments are often omitted.

The primary requirement of any modern system of furnace control will be the elimination of the necessity of physical labor by the furnace-operating crew in the management of the furnace, I-2. Thus the first step of operating improvement will be to arrange for the motivation of all heavy valves and location of the actuating means at the control board. The units specifically in mind will be the air-inlet valves (natural-draft furnaces) and the waste-heat boiler and stack dampers. Where forced or induced draft is included, adjustment of fan speeds should be arranged at the control board. All of these valves require frequent adjustments, which will be made to best advantage only if the adjustments are easily and conveniently accomplished, and it is believed to be of utmost importance to complete this fundamental operating betterment before any more forward step is attempted.

Comment on the control of the pressure of such factors of fuel practice as oil, tar, steam, and the clean cold gases is deliberately omitted, because such items are not those of control at all, but of basic plant design, and where they are absent, as often they are, the services of the plant engineer and the installation of simple equipment rather than refined apparatus of instrumental operation are prerequisite to any operating improvement.

Certain simple indicating instruments, I-3, are of great help to the operator and the following are indispensable: a large gage to indicate the quantity of fuel entering the furnace; indicators of the openings of the principal valves of the flue system; recording pyrometers showing temperature at some appropriate spot of all regenerators; recording pyrometer of the gas temperature on the cold side of a waste-heat boiler if included.

Recording and totalizing devices may be of considerable value to higher authority as a log of operation, but they are of no service to the operator.

Instrumental control as defined in II-2 may be conveniently subdivided into four parts, as follows:

1. The control of temperature through fuel input, by means of indications from furnace-gas or roof temperature.

2. The control of combustion quality, selectively through the mechanical proportioning of fuel and air or automatically by the use of furnace-gas analyzers.

3. The control of furnace laboratory pressure by the automatic control of waste gas flow.

4. The control of furnace and/or regenerator temperatures by means of automatic reversal.

Control of temperature is a comparatively recent development. It is not believed that the control of fuel input from the indication of furnace-gas temperature can prove particularly successful, for a safe flame temperature varies widely at various periods of the heat.

Infalibly to safeguard the refractories would necessitate that the instrument function from the lowest safe temperature, and this would greatly lengthen the time of heat.

The successful control of the fuel input from indications of roof temperature, for the reasons mentioned in the discussion on insulation, must include appropriate methods of modification to roof conditions.

The value of automatic control of combustion quality is variable. All mechanical systems include a method by which the ratio of fuel and air may be changed at will by the operator, and experience has shown that several changes are desirable during a heat. When fuel quality is stable, the devices undoubtedly are of some value when correctly installed, but when fuel quality varies considerably, as in firing producer gas, it is doubtful whether they are of any value.

Analyzing controls for furnace gas thus far offered have not been satisfactory, for various reasons. Aside from purely functional

weaknesses, they appear to lengthen the time of the operation. The lengthening of heating time by 6 or 8 per cent will increase capital costs to an extent that would alone wipe out a fuel saving of one-half million British thermal units.

Automatic control of pressure in the furnace laboratory offers the most interesting possibilities of improved operation, when, and if, devices are contrived to overcome the objection found in most of the apparatus now offered for this purpose. These devices react to control through the suction fan or stack damper and the governing impulse is so very small that there is too great a time lag before the device functions. By the same cause, when in operation, they are prone to overrun the correct position, with the result that they are ever in unbalanced motion. A very vital factor in the installation of draft control is the selection of the locations for the antennae.

Automatic furnace reversal is possibly the most universally successful automatic aid to furnace operation thus far introduced. At some parts of the heat, in common with every other automatic device, it must be thrown out of operation and manual operation substituted, but except in the early and final stages of the heat it can be counted upon to render valuable aid to the operators and real operating improvements.

Full automatic control, the final one of the list of control methods II-2, consists in the interlocking or interconnecting of the four principal and often several subsidiary controls in such a manner that all the various items operate interdependently of all the others. A number of such installations have been made but the results have offered little promise for the early general adoption of full automatic control.

In general, instrumental control of furnace functions has proceeded with too much speed and with insufficient soundness, and the reason for this condition lies not with the manufacturers of the apparatus, but with the open-hearth executive, who in his quest for the economy his superiors are demanding entirely loses sight of the truth that the adage, "There is no short cut to success," may be paraphrased by the alteration of the final word to "economy."

CONCLUSIONS

Improvement in furnace operation will come rapidly when the truth is driven home that before refinements to operation can be even partly successful the fundamental design of the furnace and its system must be developed until no further basic improvements can be made.

The open-hearth superintendent is essentially a steelmaker and a mighty busy man making steel in the quantity, and of the quality, specified by superior authority. The chances are he is not a physicist, chemist, engineer or economist, and when, as so often happens, he attempts to

invade their fields he can only putter. So often in the steel plant, a little knowledge is a dangerous thing.

No improvement involving the application of insulation or the installation of control should be attempted except as a part of a betterment program in which these items enter the program in a scheduled sequence. For those who would establish a betterment program that will accomplish the greatest good with the least investment in the shortest time a schedule similar to the following is suggested:

1. Critically examine the furnace and determine its fundamental faults or weaknesses.

2. Minimize the faults or weaknesses so determined with the least possible compromise.

3. Motorize the operation of all the heavy valves and locate all control means at the platform control board in order to remove the necessity of physical exertion by the first helper in the operation of the furnace.

4. Install the simple instruments that will actually aid the first helper in operating the furnace, teach him to use them, and see that he does so.

5. Insulate the upper furnace in accordance with approved methods.

6. When, and if, all concerned concede that the furnace is at the peak of operating condition, and that no further improvements are possible through redesign or rebuilding, it is in order to seek added economy of operation through the installation of the refined instruments, auxiliaries, or apparatus that take over and operate automatically one or more of the phases of operation that heretofore have been functions of the mental or ocular reactions of the man responsible for the results.

Real advantages to operation accrue from the addition of correctly applied insulation, and certain instrumental aids of careful selection, but the casual or poorly conceived application of extraneous refinements is fraught with the possibilities of costly and reactionary experience.

DISCUSSION

(Francis L. Toy presiding)

H. C. BARNES,* Middletown, Ohio. (written discussion).—As pointed out by Mr. Buell, insulation below the charging floor has been generally accepted for several years. Most of the insulation on this part of the furnace is a more or less permanent improvement, as it is not disturbed during a regular furnace rebuild. In numerous instances the actual savings from reduced air infiltration are as great or greater than the savings from reduced heat conductivity when insulation is applied below the charging floor, and the insulation used should be either impervious to air infiltration or should be backed up with an airtight metal casing.

The largest potential saving from insulation is above the charging floor, where a saving of $\frac{3}{4}$ million B.t.u. or more per ton is possible but the slowness with which insulation of this part of the furnace has been adopted is largely due to furnace outlines and dimensions frequently unsuited to insulation which led to conflicting and

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inconclusive results on the early installations. With a realization of the necessity for better flame direction, ample combustion space and practically complete combustion, consistently satisfactory results are now being obtained when these fundamental principles are observed. Since furnaces with insulation will usually have a lower fuel rate and consequently a lower combustion air input, the port construction of furnaces that depend appreciably upon the air for flame direction will require close study when insulation is applied.

There seems to be no doubt that properly insulated silica brick with a moderately high temperature throughout is more durable than bare silica brick with about 2900° F. inside temperature at one end of each brick and 500° to 600° F. at the other end, in which the crystal changes occurring at 1200° to 1400° F. move back and forth in the brick and tend to cause breakage and spawling. Insulated silica brick must be protected from direct flame impingement, since the temperature gradient through the brick is small and any overheating of the inner surface penetrates much deeper than in an uninsulated brick with a steep temperature gradient.

The refractory insulators designated as class A by Mr. Buell are almost necessary as the first insulating course on the roof if deterioration of the insulation is to be avoided after the primary roof becomes thin. Probably the best of these materials is the porous silica insulating brick now available. Outside a 2½-in. course of this material, any of the lower temperature materials with better insulating properties will stand up. If class C materials are used next to the primary silica-brick lining, great care must be used to select a material that does not decompose and has no fluxing action up to 2400° F. as this temperature may be approached at the joint between lining and insulation when the lining becomes thin.

Mr. Buell is correct in outlining a gradual development of furnace control through the stages of measuring instruments and gages for the guidance of the first helper, power operation of the heavy valves and dampers by manually operated push-button control before the final stages of automatic control of some of the regulating devices. At best, automatic control devices can be considered only as an aid to the first helper, who must frequently make manual adjustments to take care of temporary abnormal conditions.

Roof thermocouples are now available for the automatic control of furnace temperature by regulation of the fuel input, but the required fuel input is influenced by so many other factors not adapted to direct measurement that the practicability of the automatic control of this item is doubtful.

The automatic control of combustion air input to correspond to fuel input is in successful operation in a number of plants. The proportioning controls in which the measurement of cold air to the furnace is balanced against the measurement of fuel input have been highly developed, but are subject to the inherent limitation that they make no provision for air infiltration between the regulating valves and the furnace. The control of air from waste-gas analysis is fundamentally more correct and is gradually being developed into a practical method of control. Savings of 10 per cent in fuel consumption and 6 to 8 per cent increase in production have been obtained from this method of control, although these results cannot yet be always expected.

The control of furnace pressure and stack draft is becoming more satisfactory and more commonly used. The extremely small pressures to be controlled require supersensitive instruments, the perfection of which requires considerable time and experience. Instruments sensitive to 0.002-in. water pressure are now available. Probably the most satisfactory location for the pressure connection to the furnace is a tube through the water-cooled frame of the middle door.

Control of checker-chamber temperatures is in quite common use, either by temperature measurements and manual reversal or by full automatic reversal. Control

of this factor has been very effective in keeping the two ends of the furnace balanced, resulting in less erratic furnace performance.

Although much of the control equipment now available is only partly satisfactory, as pointed out by Mr. Buell, it will be necessary to continue the use of present equipment and the trial of new instruments leading toward full automatic control, in order to work out the "bugs" in present apparatus and methods, and make further progress in converting open-hearth operation from an art to a science.

Slag Control in the Making of Iron and Steel

At the fall meeting of the Iron and Steel Division, Oct. 4, 1934, in New York, a symposium was held on Slag Control in the Making of Iron and Steel. The chairman was J. H. Nead and the vice chairman, G. B. Waterhouse. The latter presided at both morning and afternoon sessions. The papers and discussions were presented in the order in which they appear on the following pages. To meet space requirements, much of this material has been considerably condensed.

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Slag Control and the Blast Furnace

BY RALPH H. SWEETSER,* MEMBER A.I.M.E.

To control the slag in an iron blast furnace is to control the quality of the pig iron produced (and to a certain extent the tonnage), and to control the whole operation of the furnace itself, including a large part of the cost of production. The character of the slag is the determining factor in the character of the pig iron as to the controllable limits of sulfur, silicon, and, to a certain extent, the manganese; it has an influence on the proportions of combined and graphitic carbons.

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The slag character depends on the kind of fuel used, as well as on the analysis of the ore burden and of the flux itself. When blast furnaces used only charcoal for fuel there was not much difficulty in slag control, because there was no trouble in making low-sulfur pig iron. But when mineral fuels, anthracite and block coal, were introduced, now nearly 100 years ago, there was plenty of trouble on account of proper slag control; they introduced the problems of sulfur elimination, hearth temperature and slag volume.

BLAST-FURNACE FUELS IN RELATION TO THE SLAG

The five principal blast-furnace fuels used in this country during about three centuries of iron smelting—charcoal, anthracite, raw coal (bituminous), beehive coke and byproduct coke—have imparted certain characteristics to the slags produced as well as to the pig iron.

The early anthracite blast furnaces were handicapped by tremendous slag volumes—the exact opposite of the charcoal furnaces—and this helped to keep down the tonnage of pig iron made; 2 tons of anthracite, 2 tons of iron ore and $1\frac{1}{2}$ tons of limestone (all gross tons) was not conducive to high tonnage and low costs. In those days when there were no chemists at the blast furnaces, much low-grade limestone was used as well as low-grade ore. The general practice of using dolomite for flux caused an excess slag volume, excess fuel consumption and decreased output without any advantage in removing sulfur.

Beehive coke had a hard time getting started as a blast-furnace fuel, but when the right kind of coal was used the progress was rapid; then when coking coals with high ash and high sulfur were used for beehive coke, a new set of slag troubles worried the blast-furnace men at the same time they were learning to use Mesabi ores.

Research work in blast-furnace slags was so meager before the World War that when the Bureau of Mines sent Alexander Feild to the Columbus blast furnaces early in 1917 it was necessary to revise the whole technique of taking samples of slag and of making the daily analyses. Since the war there has been much progress in the study of blast-furnace slags; we have passed from beehive coke to byproduct coke as the predominating blast-furnace fuel; consequently there is a change in the character of the furnace slags, especially in respect to decreased basicity and volume.

VOLUME OF THE BLAST-FURNACE SLAG

The campaign for clean coal for blast-furnace coke that was waged several years ago resulted in a considerable reduction of the weight of slag per ton of pig iron. Now we are working to decrease the amount of waste materials shipped in Lake Superior iron ores and to increase the iron content. All this is in the interest of low-cost iron and steel, but

it reacts to reduce the amounts of materials hauled from one part of the country to another, and to reduce the slag volume.

It is metallurgically sound to have the slag volume in the blast furnace as low as is possible for the elimination of impurities of the fuel and ore burden. It is not advisable to run a blast furnace *too* close to the minimum volume of slag requisite to remove the sulfur and other impurities; this is all the more true when the volume is small because a slight variation in analysis might make a great difference in the free-running temperature of the slag. When we consider a blast-furnace slag as a magma in which the various minerals and metalloids are in solution as separate compounds, we can readily see that when we have enough of the solvent there is no need in having too much; the right quantity in each case can be established by actual practice.

The compound that carries the sulfur is calcium sulfide (CaS), and the amount that can be dissolved by the magma depends on its chemical and physical make-up.

TEMPERATURE OF BLAST-FURNACE SLAGS

The melting point of blast-furnace slag is a very important factor; it depends upon the chemical composition, especially the percentage of silica, alumina and lime. The most helpful guide for slag control that I ever saw was a plaster model of the triaxial diagram of the melting points of varying percentages of silica, alumina and lime, made by Wilbur Stout when he was chief chemist for The Columbus Iron & Steel Co., long before he became State Geologist for Ohio. This model showed the necessity of burdening the furnace for a slag that has a safe margin of leeway in the variations of magnesia and alumina when working with certain iron ores, especially when the alumina is only about 5.00 per cent; each slight decrease in the percentage of alumina makes a slag of much higher melting point. A similar condition exists when there is very little magnesia in the slag.

Although the temperature of the slag inside the furnace is higher than the temperature of the pig iron, it is not economical to have a slag with a free-running temperature so high that it takes excessive fuel to melt it.

With charcoal-furnace slags the silica can be carried so high that the melting point of the slag is very low, and there is a large area of "safe" analysis. When basic iron was first made in this country it was thought necessary to carry a very limey slag so as to get low silicon and low sulfur in the pig iron. Nowadays, with low-sulfur coke and a rich iron mixture it is safe to run on a very "lean" slag without the danger of getting high-sulfur iron. Some open-hearth men say that basic iron from a furnace with a very hot hearth, which means a more refractory slag, is preferred.

VARIATIONS IN SLAG ANALYSIS INSIDE THE FURNACE

The variations in slag analysis from one side of the furnace to the other are sometimes so great that it is a wonder that it is possible to keep the furnace on such regular iron as we do. A cold steel rod pushed into the furnace through the peephole at any tuyere, and removed quickly, would have slag of different analysis for each depth of penetration into the hearth. Often there are different kinds of slag at the different tuyeres. I have removed slag from inside the hearth through the tuyeres with a water-cooled sampling pipe with cups every 12 in., and have seen the variations in slag composition.

This variation shows up at the flushes and at casting time, not only in appearance and analysis, but also in temperature, as was shown in my paper presented at the Round Table in February, 1927¹. This variation is also shown in taking samples of slag at the cinder notch, iron notch and tuyeres.

Just above the tuyere level there must be enough excess lime in the slag to take care of the residue of ash left in the coke at the time of its complete combustion at the tuyeres. With very high-ash coke this condition is objectionable and often causes serious trouble, especially when the coke is in large pieces of irregular sizes.

BLAST-FURNACE FLUX

Limestone is so widely scattered over the country that it has been usual to select the nearest flux stone that was pure enough to be used in the blast furnace; but as blast-furnace practice has become more refined it has been profitable to obtain the right kind of flux stone, even if it meant a higher cost and a longer freight haul. It has been found that the stone must be sized and cleaned. In many quarries the flux stone is washed, to remove all the fine limestone dust.

In only special cases is it necessary to have the phosphorus in the flux stone very low; in some cases it is needful to be sure that the sulfur is low. Sometimes limestone containing an appreciable quantity of zinc has caused much trouble. It has been thought that barium would be advantageous in blast-furnace flux, but, pound for pound, the carbonate of calcium is the better flux. "BaO is about one-third as effective as an equal weight of CaO in removing S and in fluxing SiO₂ and Al₂O₃."² If barium is present in the ore it is helpful, but barium in a flux stone is not worth the cost.

The fluxing of each blast furnace is a case by itself and it depends on the kind of materials used and the product made.

¹ R. H. Sweetser: Carbon in Pig Iron. *Trans. A.I.M.E.* (1927) **75**, 423.

² C. E. Wood and T. L. Joseph: Effect of Barium Oxide on the Desulfurizing Power of Blast-furnace Slags. *Trans. A.I.M.E.* (1929) **84**, 126. Iron and Steel Division.

DISCUSSION

F. B. RICHARDS, Cambridge, Mass.—They created a new industry in limestone when they found out something about the use of dolomite and the use of straight limestone. As far as coke is concerned, I think I used the first byproduct coke that was made¹ by the Solvay Company. We bought 10,000 tons of coke from the H. C. Frick Coke Co. I believe that they shipped foundry coke, bright, silvery coke pieces about a foot long. We used that 10,000 tons, and then we used 10,000 tons of the Solvay coke, made at Syracuse. There was appreciably no difference in output or working of the furnace. I think if the Frick company had shipped its straight 48-hr. coke at that time it would have been very much better than the byproduct coke. The slags were entirely different in appearance. The usual analyses were made, but in appearance the slag when using the Frick coke, which I am quite sure was 72-hr. coke, showed a marked difference as against the byproduct.

Slag Control in Rimming Steel

BY L. F. REINARTZ,* MEMBER A.I.M.E.

The furnace in which rimming steel is made has an important bearing on the quality of the steel produced.

Furnace.—Particularly in the manufacture of low-carbon rimming steels, it is necessary to have an efficient, easily regulated furnace, because of the relatively high finishing temperature requirements. In recent years, the most important development in design of open-hearth furnaces has been the sealing and insulation of the greater part of the furnace to prevent air infiltration and loss of heat. Efficient, straight-line valves insure proper draft. Combustion controls guarantee correct gas-air ratios. Furnaces of all sizes ranging from 20 to 200 tons have been used successfully in the manufacture of rimming steels. Metal bath is varied from 20 to 40 in. in depth without appreciable variation in quality.

Charging.—A normal open-hearth charge consists of pig iron (hot or cold), scrap of miscellaneous nature, and slag-making additions, such as limestone and burnt lime. Because of local conditions, some plants find it necessary to discard the use of pig iron and use some carbonaceous substances with varying percentages of cast iron to replace the pig iron. It is questionable whether such practice will consistently produce the quality of rimming steel required for auto stampings and other severe drawing requirements.

Pig Iron.—An open-hearth furnace under proper control should melt 150 tons of low-carbon rimming steel on about 35 to 38 per cent pig-iron charge basis. In some practices, best results are obtained when the total charge contains from 0.40 to 0.50 per cent silicon. If reasonably low-

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silicon scrap is available, pig iron should contain from 1.00 to 1.30 per cent silicon, as well as under 0.035 per cent sulfur, under 0.300 per cent phosphorus, and about 1.50 per cent manganese.

The closer a blast-furnace operator can keep to the desired analysis, the more uniform will be the product of any well regulated open-hearth plant. It has been definitely proved in certain plants that if a heat melts with over 0.20 per cent residual manganese in the bath, good rimming results are difficult to obtain.

If the iron is to be used "hot," great care should be exercised to see that the blast-furnace man taps his iron physically "hot." A number of plants have found that iron tapped physically "cold" from the blast furnace and used in rimming-steel heats causes them to melt "dead" in the furnace. Even if the heat melts with carbon, there is a tendency for it to drop very rapidly. The heats pour sluggishly, and blisters and laminations can be expected.

Scrap.—Not much care can be exercised in scrap selection. The kind of scrap available often depends on the location of a steel plant. If considerable scrap from "killed" steels must be used, it will be necessary to reduce the silicon in the pig iron. If the scrap is all low-carbon rimming steel, the silicon may have to be raised in the pig iron to about 1.40 per cent to balance the total silicon in the charge. In order to maintain uniformity in charging and melting conditions, it is advisable to charge as closely as possible the same percentages of each grade of scrap from heat to heat. This cannot always be done in some plants, because of the plant layout. Such a plant will operate under a distinct handicap. It stands to reason that mixed quantities of alloy, galvanized, painted, or badly corroded scrap are objectionable. Silicon-steel scrap should be kept out of rimming steel if at all possible.

Flux.—In making slag for rimming steel, the flux is very important. The metallurgist and operator must decide how to hit a "happy medium" between speed of melting and quality of ingots produced. Limestone or burnt lime, or a combination of both, are used as fluxes. Many plants use a burnt lime flux charge. There is a distinct impression, however, that steel that must be coated should be made out of all raw limestone in order to cause more action in the metal bath. In limestone, the silica and magnesia should be kept as low as possible for best results. In preparing the scrap for a charge, it is necessary to make up the bottom rapidly to conserve heat. Care should be taken that the bottom has been thoroughly drained. All puddles of steel from preceding heats should be cleaned out. Clean bottoms are essential for the best quality of rimming steel.

Charging Practice.—The most efficient practice is to charge the heat as rapidly as possible and get it "under cover" in the minimum time. Here is where a sharp, well controlled furnace pays dividends, and this is the

only stage of the heat that can be rushed without detriment to quality of the steel.

Refining Practice.—After a heat is “under cover,” the furnaceman must watch it closely as it melts. For best average results, it is well to have the heat proportioned so that it will melt between 0.30 and 0.50 per cent carbon at this point. If the heat begins to melt with higher carbon; lump ore may be added to bring the carbon down. If the heat appears to be melting with little carbon, it is best to add “cold” pig iron or some “hot” metal at this point, to raise the carbon sufficiently so it will be possible to “ore” the heat after the bath is entirely melted.

When the limestone comes up through the bath, it may lie on top of the metal in a viscous mass. It is advisable to “cut up” the lime by the addition of fine ore or scale. Spar should be used sparingly and in small quantities at each addition. Too much spar makes “wild watery slags” at the end of the heat, which, in turn, means oxidized steel in the metal bath, loss of yield, and a product of poor quality.

The percentage of limestone or lime to be used has been the cause of controversy among open-hearth men for many years. If the silicon and sulfur analyses of the charge of a low-carbon steel heat were accurately known before each heat was charged, it would be reasonably simple to proportion the lime in a heat according to the impurities to be removed. Usually, these factors are not known within close limits. In most cases, 6 per cent limestone or 4 per cent burnt lime will take care of the non-metallics in a bath of rimming steel. However, we must remember that the bath must be protected from overoxidation of the flame and, therefore, it is advisable to add enough additional lime to give sufficient bath coverage for this purpose. For deep-drawing steels it is preferable not to use all burnt lime in the charge.

Iron Oxide Control.—When making 0.10 to 0.15 per cent carbon steels, good practice in some shops is to try to have 18 to 23 per cent FeO in the slag at tap. If the heat is to finish with 0.05 to 0.07 per cent carbon, the FeO in the slag should be 30 to 35 per cent. If the iron oxide is higher than the figures given, the slag will be too thin, and excess deoxidizers will be needed when the heat is tapped. If the iron oxide is much lower, the slag will not contain enough iron oxide to produce the proper rimming action in the molds. It is difficult to correct the high iron oxide condition, but if the iron oxide is too low the percentage can be increased by judicious additions of fine ore or scale.

Clean ore must be used for regular “oreing” practice. In removing carbon from a bath, lump ore is more efficient than fine ore. The carbon should be “ored” down to within a few points of the desired carbon and then “oreing” should cease. The last few points of carbon may be “poled” out with wooden poles or steel bars. It is better to add small charges of ore than to put in a large charge and freeze up the bath. A

practical slag analysis for low-carbon rimming steel of about 0.06 per cent carbon analysis is as follows: 10 to 14 per cent SiO_2 , 22 to 29 per cent FeO , 5 to 9 per cent Fe_2O_3 , 38 to 40 per cent CaO , 7 to 8 per cent MnO , 8 to 10 per cent MgO , 1 to 2 per cent Al_2O_3 , and 1 to 2 per cent P_2O_5 .

The slag should be slightly thickened at the end of the refining period with burnt lime to insure a creamy slag. If a low-carbon heat has been properly proportioned so that it does not melt too high or too low, and scrap charge of about the same analysis is used, it is possible to melt and tap the heat with reasonably close control of iron oxide in the slag. From these figures, it is possible to check closely from heat to heat the amount of deoxidizer necessary to add to the ladle. Care should be taken to keep the metal "hot" during the refining stage, so that at the finish it will not be found necessary to ruin the slag by overheating it in order to bring the metal up to temperature.

Tapping Practice.—At tap, the heat described above will contain about 0.08 to 0.12 per cent residual manganese. A slag test is run just before tapping to indicate the iron oxide in the slag. Manganese and deoxidizer additions are figured on the basis of this analysis. A good practice in the manufacture of 0.10 per cent carbon steel is to add one-half of the ferromanganese in the furnace in about 10-lb. lumps. The balance is added in finely crushed form in the ladle. The addition of silicon in the ladle in any form should be avoided.

In making low-carbon steels, all manganese may be added in pea size to the ladle. The temperature of the metal in the furnace must be kept within very close limits. If the heat is tapped too "cold," the metal will be "wild and gassy" in the molds. If the heat is poured too "hot," the metal will rise in the mold. Both conditions cause quality troubles later on. An expert melter can tap heats regularly with less than 50°F. difference from heat to heat. The charge should be figured so that when tapped into the ladle very little slag will be left on top of the ladle. This will prevent slag "boils" while pouring. Close attention to the details of preparation of the ladle and stopper rod and equipment will pay big dividends in the mental poise of melters and pit men, and the average quality of product over a year's period.

Deoxidizers.—The deoxidization of metal in the ladle may be carried on by the addition of aluminum in small quantities or a mixture of ferrotitanium and aluminum; both practices give good results. Most plants slightly underdose the metal in the ladle and even up by small additions of aluminum in the molds. The less aluminum used in the molds, the better. During rimming action the metal should drop in the molds several inches after the mold is filled and then rise slowly to fill the pipe. Molds should be clean and hand-warm for best results. A mold coat, such as graphite or tar, will help improve the surface of the ingot.

Conclusion.—The successful manufacture of rimming steel depends on uniformity of charge from heat to heat, close attention to good melting and refining practice, as well as pit practice, and judgment in the addition of deoxidizers to the ladle and the mold.

Slag Control Applied to Low-carbon Steel

BY FRANK G. NORRIS,* MEMBER A.I.M.E.

Slag control is adjustment of the composition of the slag, especially with respect to the FeO content. The theoretical method of slag control would be to charge a mixture of pig iron and scrap of given composition into the furnace, to melt always at the same carbon, and, after a uniform ore addition, to tap with a constant slag composition. Such conditions are not even approximated. Both scrap and pig iron are of variable, and, in many cases, unknown composition. The charge is oxidized to a variable extent during melting. The result is that the FeO content of the slag, and consequently of the metal at tap, varies over a wide range. In order to make a nearly uniform product, this variation must be compensated for in some way. One way is to adapt the ladle deoxidation to the requirements of the metal. The other is to control the slag. In a general sense slag control may be considered as a method of compensating for variations in the composition of the charge and in oxidation during melting.

The method of slag control for low-carbon steel was developed by Dr. Herty at our Butler plant³. Use of this method enables the furnace operator to tap heats at a more nearly constant FeO content and, therefore, to use a more nearly uniform deoxidation practice. The desired FeO and the accompanying deoxidation will depend on the application of the product. This statement implies that 0.10 carbon steel finished with a 15 FeO slag may be essentially different from a 0.10 carbon steel finished with a 30 FeO slag.

In making low-carbon steel, the desired carbon places a lower limit on the FeO content of the slag, because the slag must be sufficiently oxidizing for proper carbon elimination. With this degree of oxidation, the phosphorus specification is met without difficulty, and there is little danger of phosphorus reversion. Thus a limiting factor in high-carbon heats is of slight importance in low-carbon heats. For heats of 0.05 to 0.07 per cent carbon, the FeO content of the slag may be controlled at

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³ Our research laboratories have been interested in slag control for many years. Dr. Herty has recently cooperated with our operating and research divisions at our Butler, Pa., works in studying slag control in rimming steel from a scientific and practical standpoint. L. F. REINARTZ.

any desired value within the range 13 to 35 per cent FeO. The Fe_2O_3 content will be in the range 6 to 12 per cent.

The basis of slag control is the observation that the silica content of the slag influences the effect of a given oxidizing condition. Either an ore addition or the furnace atmosphere is less effective in increasing the FeO content of a high-silica slag than of a low-silica slag. Study of heats during periods of no carbon elimination shows that with about 15 per cent silica there is little change in FeO. With less than 15 per cent silica, which is the usual condition at the end of the heat, the FeO increases as the heat is held. With more than 15 per cent silica, the FeO decreases during the holding period.

The application of this principle depends upon the conditions of the heat being made. If low FeO be desired, the silica content of the slag will be kept as high as possible during the entire period of the heat and especially before the ore addition. The practical limitation to the silica content is that it must not be high enough to cause damage to the slag line or to cause too high sulfur in the metal. With a high-silica slag, carbon is eliminated to the desired value at a lower FeO in the slag than with a low-silica slag, because for a given FeO in the slag the FeO in the metal is higher with high silica. Under a slag containing 30 FeO and 10 per cent silica, the metal will contain 0.20 per cent FeO; with a slag containing 30 FeO and 20 per cent silica, the metal will contain 0.37 per cent FeO. The apparent effect of this difference is that a high-silica slag will not hold the ore, but allows it to work directly on the metal. When the slag contains low silica, the heat should be tapped as quickly as possible to avoid an increase in FeO during the period of holding under a low-silica slag.

If control involves increasing the FeO, the silica is kept low during the entire working period. The slag is allowed to become heavy early in the heat. Spar should be used sparingly if at all. If the slag becomes too heavy or mucky, it is preferable to cut it with ore. If the slag should become too thin, more lime should be added. The lime should be added before ore because this makes the ore more effective in raising the FeO content of the slag. For this type of heat, fine ore or clean mill scale is preferable to lump ore. Scale has a lower melting point than ore and is more easily dissolved by the slag. The requirement of the heat should be anticipated as early as possible. Usually from 250 to 300 lb. of scale will increase the FeO in the slag one per cent. The exact increase in FeO from a given scale addition will depend on the slag weight and the extent of carbon elimination. If the scale is added in several batches, the desired final FeO can be attained with remarkable accuracy. The last scale addition should be 30 minutes or more before spiegel. Preferably, the FeO should not be changing rapidly when the spiegel is added.

These principles apply to every heat. The details of the application will vary from heat to heat and cannot be stated definitely in advance, but must be planned as the heat is being made. Likewise a detailed review of past heats is only a general indication of how to get similar results in future heats.

DISCUSSION

R. H. SWEETSER.—Mr. Reinartz spoke of slag containing 18 per cent FeO . I think he expressed the iron as oxide. I should like to ask at what point, in iron contents, it is usual practice to quit sending that open-hearth slag to the blast furnace?

L. F. REINARTZ.—No problem is involved in disposing of open-hearth slag to our blast furnaces because, on account of the grades of iron and steel made by our company, the iron oxide in the slag is sufficiently high to make it very acceptable to the blast-furnace operator. I have been told that if the total iron oxide in the slag is under 18 to 20 per cent, it is not economical to use such slag in a blast furnace.

J. T. MACKENZIE,* Birmingham, Ala.—Mr. Reinartz mentioned sulfate in the limestone. I wonder if he did not use the wrong word. We always have assumed that the sulfate sulfur is practically harmless. Most limestone carries some pyrite (sulfide sulfur) which we thought was what gave the sulfur pick-up.

L. F. REINARTZ.—I have had no experience, personally, in the use of limestone high in sulfates. I have been told, on several occasions, by other open-hearth men, that the sulfates will be reduced and increase the sulfur content of the metal. We have never found any pyrite in our limestone.

A. HAYES,† Middletown, Ohio.—I should think that sulfates would be readily reducible to sulfites, and possibly to sulfides at various distances through the slag layer, from the top down to the interface between the bath and the slag, because reducing conditions are certainly sufficiently strong next to the bath in the slag to reduce sulfates to sulfides.

A. L. FIELD,‡ Baltimore, Md.—What is Mr. Reinartz's theory as to the effect of silica in the slag on the iron oxide content of the metal?

L. F. REINARTZ.—I have no particular theory as to the effect of silica in the slag on the iron oxide content of the metal. I know from practical experience that it does have an influence on reduction of iron oxide in the metal. We know that if the silicon content of the charge, and, therefore, the silica of the slag is increased, the iron oxide in the slag will be decreased. Based on Dr. Herty's work, we assume that the iron oxide is correspondingly decreased in the metal.

C. H. HERTY, JR.,§ Bethlehem, Pa.—In the theory of iron oxide control, we have tackled the matter from the physical standpoint, rather than the chemical standpoint or from the slag itself, and we worked on the basis that the change in iron oxide content in a slag—that is, whether the slag increases or decreases in iron oxide—is due to the simple fact that if you put more iron oxide into the slag from the gas than you put oxygen from the slag into the metal, the slag must increase in iron oxide;

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† Director, Research Laboratories, American Rolling Mill Co.

‡ President, Alloy Research Corporation.

§ Research Engineer, Bethlehem Steel Co.

whereas if you put more iron oxide into the metal from the slag than you can get from the gas, the slag necessarily must decrease in iron oxide. That nobody can argue with; that is just fact.

Early in our slag work we found that the higher the silica in the slag, the more rapid the transfer of iron oxide to the metal relative to the transfer from the gas to the slag, and therefore, with high-silica slags we found that the iron oxide in the slag tended to decrease; with low-silica slags it tended to increase; and in order to tie that point up with our theory of input and output and slag analysis, we determined the relative fluidities of very basic, weakly basic, and fairly acid open-hearth slag in the viscosimeter, which is described in one of our bulletins, which will be published soon.

The principle is simply this, that if we pour a sample of slag into a casting that has a long horizontal hole in it, the more fluid the slag and the greater the superheat, the farther it will run out into the hole. With a very viscous slag it will run out very little.

In order to get the temperature effect, which was what we were interested in, we took samples of slag out of the furnace and held them for various lengths of time, then poured them into this casting, the presumption being, of course, that the longer a spoonful of slag is held, the lower the temperature will go. So we were measuring, in some sense, the change in viscosity of the slag with temperature, and we found (I will read you the relative viscosities, because they are the key, I think, to the situation) that with a slag that runs 28 per cent silica and 33 per cent lime—that would be early in a heat, of course—if the fluidity was one as the slag was taken out of the furnace, it would have dropped to seven-tenths at the end of 60 seconds in the spoon. In other words, there was only a slight drop in fluidity with temperature on that very acid slag. But with the more basic slags—say 19 per cent silica and 46 per cent lime; that is beginning to be a pretty basic slag—we find that in 15 seconds the slag cannot be poured, and that there is a regular change in fluidity against time with slag composition. Furthermore, that after thinning out a heat with spar, we begin to get something of the same fluidity-temperature effect as with a higher silica slag.

In the open hearth, as long as the metal is being heated up, it is obvious that the upper layer of slag, the slag-gas interface, is at a higher temperature than the slag-metal interface. Therefore, in an acid slag these data would indicate only a slight change in fluidity from top to bottom of the slag, but as the slag became more basic, the temperature at the slag-metal interface, the lower temperature, would cause the slag to be more viscous there. So that with an acid slag there would be an easy transfer from slag to metal compared to the gas. With basic slag it would be difficult to transfer it, on account of the increased viscosity. Therefore, using those two slags relatively, the acid slag should lose iron oxide when the basic slag was gaining, or in any event, the basic slag should gain iron oxide faster than the acid slag.

We have checked that up on high-carbon and low-carbon heats, and we have yet to find an exception. In other words, as the slag changes composition and fluidity, the pounds of iron oxide in the slag, which is really what we are interested in, changes regularly with slag composition and slag fluidity, indicating that what we are really interested in is the effect of silica on fluidity rather than on any chemical composition. We have studied that on 60 to 80 carbon steels at Edgewater, and on 0.04 to 0.06 carbon steels at Butler, and both sets of data, the high and the low carbon, fall in beautifully.

So that, to my mind, is the theory of why an acid slag tends to lose oxygen and a basic slag tends to increase in oxygen.

As to Mr. Feild's other question, regarding the relative amounts of iron oxide in the metal under an acid and a basic slag, I believe that is very simply answered by the fact that is pretty well known, that Fe_2O_3 increases as lime goes up, indicating a

formation of some calcium ferrite, and there has been some recent work in Japan which shows the calcium ferrite to be fairly stable at high temperatures. So as it becomes more and more basic, more and more of the iron oxide in the slag would be unavailable for oxygen. So your slag with 30 per cent iron oxide, as Mr. Reinartz showed, would contain more iron oxide in the metal for a siliceous slag than it would for a very basic slag, because there is more active iron oxide in the siliceous than in the basic slag, owing to the formation of some lime-iron oxide compound.

If you take the fluidity and the viscosity of the slag into account and work the heat accordingly, it is very simple to control iron oxide. On the high-carbon heats at Edgewater we were able to make two series of heats—one aiming at 7 per cent FeO. The FeO I am talking about now is not total FeO; it is actual FeO, because at that time we were determining Fe_2O_3 , one series of heats where we aimed at 7 per cent FeO and another at 6 per cent FeO, and our first maximum range was 6.11 to 7.75 over a series of heats. In the second series we aimed at 6, and with the exception of one heat, our deviation was 5.81 to 7.07. In other words, by using that concept of changing the slag, we were able to control the high-carbon heats very, very closely; and on the low-carbon heats, using the same method as a guide, we made a series of what Mr. Norris called low iron oxide and high iron oxide heats, and the data for those, although not so close as the high-carbon heats, was nevertheless very good, because we found that we were able, in making a 20 to 25 per cent total FeO, in this case on low carbon, in every heat we made to stay in that limit, and on the high iron oxide heats, the 30 to 35 per cent total FeO, we hit 7 out of 8 consecutive heats in that, and the heat we did not hit came $28\frac{1}{2}$. So, using our slag analysis and viscosity in making our additions, depending on what had happened earlier in the heat as to composition and viscosity, we were able to hit very nicely.

I think the whole theory of slag control is tied up in the question of silica and its effect on the fluidity of the slag, and the transfer from gas to slag and from slag to metal, the relative transfer, and on that basis the heat can be controlled just about as you want it.

Mr. Reinartz's opening sentences on the practical observations are probably by far the most important in iron oxide control, and that is, to give the furnace a charge that will bring it to a given FeO, instead of having to worry all the way through a heat. In other words, by charging the furnace properly, you can hit pretty closely within a certain FeO, and then when the pig iron goes off or the scrap gets back, you can fall back on control methods in order to bring back whatever iron oxide you want.

The two main results obtained from iron oxide control are: First of all, until you are able to control iron oxide to fairly narrow limits you are really not able to say what is the best iron oxide. In other words, I never have seen any data yet where you can go to a series of random iron oxide heats and pick out, say, 16, 18 or 12 per cent as the best condition. About the only way to get it is to make a consecutive series of heats. In other words, fill up the mill with low iron oxide heats, or high or medium, and then see how that change is going to affect you all the way down the line, because I think the oxidation of the slag goes much further than the rimming action in the mold, and goes on down into the finished product.

The second thing, of course, is that once the proper point for iron oxide control is determined, you are able to control it consistently; if you find that you need a low iron oxide, you can manipulate the furnace so that you can go ahead with much lower costs than with a random distribution of iron oxide or with high iron oxide.

Slag Control for Basic Open-hearth High-carbon Steel

BY W. J. REAGAN,* MEMBER A.I.M.E.

All of the material described in the following paper is within the following specifications: carbon, 0.50 to 0.85 per cent; phosphorus and sulfur, 0.04 per cent max.; manganese, 0.60 to 0.85 per cent; silicon, 0.20 to 0.30 per cent. Steels with much lower carbon contents can be handled in exactly the same manner.

One of the first things necessary to basic open-hearth slag control is uniformity of charge, particularly as to the silicon content and the percentage of lime charged. Our past work has shown that the silicon content of the charge is more important than the carbon content in determining the carbon at which a heat will melt. We have found that by keeping the silicon content of the charge about 0.60 to 0.65 per cent, and with a lime charge of about 7 per cent (limestone equivalent), our heats melt sufficiently high in carbon to allow a moderate feed of ore and the slag will be of low iron oxide content. In making a heat of 0.75 carbon steel we endeavor to have the heat melt at about 1.20 per cent carbon.

The iron oxide content of the finishing slag depends upon the final phosphorus desired; for a given ratio of lime-silica in the slag, the lower the phosphorus desired in the final steel, the higher the iron oxide content of the finishing slag must be.

By reducing the lime charge to a minimum, the heats melt faster, and by keeping the silicon content at the desired figure the heats melt with a high SiO_2 slag, which has been shown in previous work to give a low iron oxide slag.

In most of our work, using a 180,000-lb. charge and with basic pig containing about 1.20 per cent silicon, we use a lime charge of 8500 lb. of limestone and 2000 lb. of burnt lime. The pig charge is about 48 per cent of cold pig, and the charge contains a large percentage of works scrap. This causes a heat to melt with about 1.20 to 1.30 per cent carbon, for a heat that will finish about 0.75 per cent carbon. This gives a heat that will need a feed of about 2000 lb. of ore, and also a slag with an FeO content of about 4 to 5 per cent at melting. The additional FeO obtained from the ore addition will bring the FeO in the slag at tapping to about 6 to 7 per cent. It is necessary to carry quite a fluid slag to prevent pickup of FeO , as a too heavy slag causes FeO to build up in it, giving a finishing slag with a greater FeO than is desired.

By adjusting the lime charge of a basic open-hearth heat, a very sensitive adjustment of the slag may be obtained. The figures in Table 1

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show just what happens when an adjustment of only 500 lb. of burnt lime is made. The pig and scrap charges on the two groups shown are very similar, the group with the lower lime charge having a slightly lower percentage of pig in the charge.

TABLE 1.—*Record of 100 Consecutive 90-ton Heats on the Same Open-hearth Furnace*

| | First Group | Second Group |
|---|-------------|---------------------------------------|
| Number of heats..... | 50 | 50 |
| In charge: | | |
| Limestone, lb. | 8,500 | 8,500 |
| Burnt lime, lb. | 3,000 | 2,500 |
| Basic pig, per cent. | 44.83 | 44.75 |
| H. M. scrap, per cent. | 22.76 | 22.73 |
| Esco. scrap, per cent. | 32.40 | 32.38 |
| Total weight of charge, lb. | 9,019,070 | 9,007,100 (finals not |
| Extra burnt lime added, lb. | 265 | 543 included) |
| Heats with no extra lime, per cent. | 72 | 46 |
| Average spiegel added, lb. | 1,980 | 1,940 |
| Average 50 per cent silicon added, lb. | 1,000 | 1,000 |
| Average Fe-Mn added, lb. | 750 | 606 |
| Average time charge to tap. | 10' 49" | 10' 48" |
| Average FeO before spiegel, per cent. | 15.10 | 12.44 (FeO plus 1.35 × |
| Residual manganese..... | 0.39 | 0.44 Fe ₂ O ₃) |
| Final carbon average..... | 0.67 | 0.68 |
| Final phosphorus, average..... | 0.020 | 0.021 |
| Final manganese, average..... | 0.67 | 0.66 |
| Average yield, good ingots, per cent. | 88.57 | 90.93 |
| Furnace loss, per cent. | 6.92 | 5.50 |
| Runners, sprues, etc., per cent. | 4.51 | 3.57 |
| Carbon at melting, average, per cent. | 1.18 | 1.20 |

As a direct result of the reduction in lime charged we find in the second group of heats that the FeO content of the slag has been reduced from an average of 15.10 per cent to 12.44 per cent and the residual manganese has been increased from 0.39 per cent to 0.44 per cent. The effect of the increase in residual manganese can be noted in the decrease in the final ferromanganese addition from 750 to 606 lb. In a number of heats in the second group the original lime charge was not sufficient to give the slag the desired basicity and additional lime had to be added. On this group of heats, instead of saving the original reduction of 500 lb. of burnt lime, we save only 222 lb., as the average final burnt lime addition on the second group of heats was 543 lb. while on the first group it was but 265 lb. It is important that the original lime charge be kept at a minimum and any lime necessary can be added after the heat is melted, such additions being determined by the slag fluidity or by the preliminary phosphorus content of the heat at melting. The ratio of CaO to SiO₂

determines the slag fluidity and the fluidity determines whether or not FeO is picked up, reduced or remains neutral in the slag, a high ratio of CaO to SiO₂ causing FeO to build up in the slag while a low ratio gives a more fluid slag and a consequent reduction of FeO.

The increase in yield on the second group of 50 heats, converted into tonnage, amounts to 63 tons, or 1.42 per cent. In other words, we get an increase in yield amounting to approximately one heat in fifty at no extra cost; in fact, at a reduced cost. The total reduction in cost due to increase in yield, decrease in Fe-Mn used, decrease in lime, etc., amounts to about 0.33 cents per net ton. We also have an intangible saving resulting from the uniformity of heats made with slag control. A glance at the figures shown, time charge to tap, carbon at melting, etc., will soon verify this fact.

In addition to a material saving in money, we have, of course, a cleaner steel made under low iron oxide slags. Six heats made under low iron oxide slags were compared with six heats made under high iron oxide slags. Table 2 gives data obtained from this test.

TABLE 2.—*Comparison of Heats Made with Low and High Iron Oxide Slags*

| Number of Heats | Average Analysis, Per Cent | | | | | Total FeO, Per Cent | Average Percentage of Inclusions by Inclusion Count |
|-----------------|----------------------------|------|-------|------|-------|---------------------|---|
| | C | Mn | P | Si | S | | |
| 3 | 0 57 | 0 69 | 0.031 | 0 28 | 0 018 | 10 41 | 0 009 |
| 3 | 0.78 | 0 67 | 0.023 | 0.26 | 0.018 | | |
| 3 | 0 60 | 0 67 | 0.028 | 0.20 | 0 018 | 15 45 | 0 0155 |
| 3 | 0 78 | 0 66 | 0.025 | 0.20 | 0 018 | | |

On the high FeO heats the percentages of large inclusions are far greater than on low FeO heats. The percentages of inclusions over 15 square divisions on a $\frac{1}{20}$ -in. grid at 200X are: low FeO heats, 0.0007; high FeO heats, 0.0028. The same groups of heats show similar results when sampled for cleanliness by the electrolytic method.

In the use of any slag-control method no hard and fast rules can be made. In addition to the charge other factors have an appreciable effect upon slag analysis, such as bottom-making materials, etc. By gas analysis of the furnace atmosphere on a great number of heats, we have found that as long as a flame is oxidizing it has no effect upon the slag. In the early stages of a heat, at which time it is impossible to obtain slag or metal samples, it is probable that the character of the flame may have considerable effect upon the slag composition. However, for all practical purposes, control of the silicon in the charge and of the amount of lime charged will control in good shape the final slag desired.

Just where the reduction in lime charge stops depends upon the conditions found in the individual shop.

DISCUSSION

C. H. HERRY, JR.—As far as I can see, from the work we did in the Pittsburgh district, the main difference between the forging grade, the so-called 30 to 50-carbon forging grade and the 60 to 80, as described by Mr. Reagan, is primarily simply a change in the level of FeO desired in the final slags. In other words, a somewhat higher iron oxide must be carried on a 30 to 50 carbon than on a 60 to 80, and Mr. Reagan pointed out the factor that ultimately limits the iron oxide. The higher the phosphorus in the pig iron, the higher the iron oxide has to be in the finishing slag, in order to stay under specifications.

In addition to the phosphorus content of the metal, there are a number of other things that may determine the required iron oxide. The first is that the iron oxide that will give the maximum cleanliness in steel is not necessarily the lowest iron oxide that can be carried. That depends a great deal on the method of deoxidation employed. Mr. Reagan uses a high-silicon spiegel, but his residual manganese is so high that he cannot use as much silicon in that as the average man uses in making forging-grade steels. So that he does not have the problem of phosphorus reversion, and consequently, because of the smaller amount of high-silicon spiegel that he uses, compared to a person making lower carbon steels, he has a different kind of inclusion problem from that of the 30 to 50-carbon steel man.

I have in mind one group in which the members have thoroughly decided that with a deoxidation practice quite different from Mr. Reagan's they prefer to have 16 to 19 per cent total iron oxide, instead of Mr. Reagan's 12, simply from the standpoint of cleanliness, not from the standpoint of phosphorus at all, because they can get by with phosphorus at 12 to 13 per cent iron oxide, but from the standpoint of cleanliness; with their method of deoxidation they have to carry, as they have found, a good deal higher iron oxide slag.

So that I think you can put down one point on slag control on forging-grade steels, that every deoxidation practice you employ probably has its optimum iron oxide content. If you are using 14 per cent silicon and spiegel, that is one thing; if you are using silicomanganese, that is another. If you are taking heats out straight, it is quite a different proposition. Each method of deoxidation has its best content of iron oxide in the slag from the standpoint of cleanliness alone.

Then we come down to the proposition of grain-size abnormality and what not, all of which are influenced to a certain extent by the combination of iron oxide in the slag and method of deoxidation employed. That is an awfully long story, and I doubt whether we can get the complete answer yet by any means, but for forging-grade steels, I think these four things are primarily the ones we are interested in: (1) the phosphorus content allowable, (2) the cleanliness, which is influenced by the iron oxide in the slag and the deoxidation method employed; (3) such specifications as grain size abnormality and (4) the other specifications that are coming into vogue.

C. D. KING,* New York, N. Y.—Mr. Reagan pointed out the economy obtained by the lower lime charge, which I think was correctly attributed to increased ingot yields, lower manganese required, improved practice, and improved metallurgical control. I believe the pig iron and raw materials in general are strikingly uniform, both in analyses and percentages used per ton of ingots, in both groups studied. The analyses of the finished steel in both groups are practically identical. Since the

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metalloids in both are practically the same and the final analyses of the steel the same, the increased yield must necessarily come about by differences in the amount of scrap produced, differences in the amount of iron lost in slag, or other slight differences. Mr. Reagan states that the scrap produced is identical, therefore we must allow for slag volumes and differences in slag analyses, apart from the small difference in manganese residual, amounting to 0.05 per cent. It is difficult to understand how a small difference of 3.00 per cent FeO in slag can account for a difference of 1.42 per cent in ingot yield, minus 0.05 per cent, the latter being higher manganese residual. The slag weights must necessarily be enormously different in the two groups to account for this very high increased yield due to this small difference in iron oxide content of the slag.

L. F. REINARTZ.—I am sure we have all been interested in hearing Mr. Reagan tell about slag control in making high-carbon steels. Probably his plant is the only one in the country that can use such extremely low iron oxide content in open-hearth slags. Any plant making a variety of steels, ranging from low-carbon to high-carbon, will have difficulty in following such a practice because of bottom and bank oxidation and other causes. Mr. Reagan, for the most part, uses high-carbon "killed" steel scrap. This scrap, together with relatively high-silicon pig iron, makes it possible for him to maintain such a very low iron oxide in his slags. In other plants, high-carbon heats of the analysis Mr. Reagan has quoted will have at least 10 to 15 per cent ferrous oxide in the slag. Good results are reported from such practice.

Slag Control for Recarburized Rail Steel

BY A. P. MILLER* AND T. S. WASHBURN,† MEMBER A.I.M.E.

Improved procedure in the manufacture of rail steel has come as the rail user demanded better wearing qualities combined with greater unit weight. With each weight increase per lineal yard has come greater difficulty in making a product that would successfully withstand all tests that modern rails must meet. With these facts in mind, and with a sincere desire to produce a rail whose service in track would be satisfactory in all respects, the steelmaker was quick to realize that all of the factors entering into his process would have to be more closely controlled. Control of rail-steel slags was recognized as one of the most important of many interdependent factors.

The object of slag control is to hold the slag compositions within a range that gives the best results with respect to economy of production, uniformity of analysis, and quality of the finished rails. The most important component of the slag from the standpoint of these production and quality factors is the ferrous oxide content. This component is a good indicator of the basicity and oxidizing power of the slag, and these largely govern the effect of the slag on the steel. Consequently, the

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control of slag composition is principally concentrated on the control of its ferrous oxide content, and the desirable range of slag composition has been determined by studying the relation between the ferrous oxide content and the production and quality factors.

Table 3 shows the relation that has been found between the ferrous oxide content and the yield. The yield figure given here is obtained by dividing the weight of the ingots and butts produced by the total metallic charge.

TABLE 3.—*Relation between Yield and FeO Content*

| Average FeO in Slag, Per Cent | No. of Heats | Average Yield, Per Cent |
|-------------------------------|--------------|-------------------------|
| 9.0 | 42 | 92 1 |
| 12.0 | 72 | 91 9 |
| 15.0 | 30 | 91 3 |

These results show a consistent decrease in the yield with increasing iron oxide content of the slag. Obviously this is due to the fact that more of the iron from the charge is taken up by the slag, both with respect to the percentage and also the slag volume, as the latter increases with the ferrous oxide. Consequently, from the standpoint of ingot yield, it would be desirable to maintain the ferrous oxide in the slag as low as possible.

There are other factors, however, that limit the minimum ferrous oxide for recarburized rail-steel slags. One of the most important of these is the factor of phosphorus elimination. The distribution of the phosphorus between the slag and the bath is affected by both the iron oxide content and the basicity of the slag. These usually are dependent variables, the iron oxide increasing with the basicity, and only the iron oxide need be considered from the standpoint of slag control. It has been found that slags with over 10 per cent ferrous oxide will maintain the phosphorus content of the bath under 0.010 per cent and will remove up to 25 per cent of the phosphorus in the recarburizing addition. With 9 to 10 per cent ferrous oxide in the slag the phosphorus in the bath begins to increase, and little or no phosphorus is removed from the recarburizing addition. With the ferrous oxide under 9 per cent the phosphorus in the bath begins to increase rapidly with decreasing ferrous oxide, and when the recarburizing addition is made there is no phosphorus removed from the recarburizer by the slag, and often a reversion of phosphorus from the slag to the bath occurs, due to the effect of the recarburizer in decreasing the basicity and iron oxide content of the slag. Consequently, for the production of rail steel with a satisfactory phosphorus content, it is necessary to maintain the ferrous oxide content of the slag over 9 per cent, and preferably over 10 per cent.

The maximum limit of the ferrous oxide is determined not only by the consideration of yield, which, as we have noted previously, decreases with increasing ferrous oxide content of the slag, but also by the factors of uniformity of ladle analyses, ingot segregation, and cleanliness of the finished steel.

The ladle analyses of a group of heats can be held more uniformly to the mean of the analysis range of the specification if a uniform ferrous oxide content is maintained in the slag. This is due to the fact that there is less variation in the efficiencies of the additions. The variation in efficiency is most noticeable with ferromanganese, the recovery from this addition being particularly erratic when the ferrous oxide in the slag is high. The following tabulation of 73 heats made to the same specification demonstrates this condition.

| FeO RANGE, PER CENT | AVERAGE VARIATION FROM MEAN OF SPECIFIED MANGANESE RANGE, PER CENT MN |
|------------------------|--|
| Under 10... .. | 0.057 |
| 10-15... .. | 0.040 |
| Over 15... .. | 0.096 |

The control of ingot segregation, for a given mold and yield practice, consists primarily in controlling the degree of deoxidation. This in turn depends on the oxidation of the bath and the deoxidation practice in the furnace and ladle. In heats with slags high in ferrous oxide, the difficulty of deoxidizing the steel satisfactorily is increased and heats of this type are often associated with segregation and decreased ductility of the "A" rails.

There is also some relation between the iron oxide in the slag and the sum of the silicon and manganese oxides in the steel, as shown by Table 4.

TABLE 4.—*Relation between FeO in Slag and SiO₂ + MnO in Steel*

| Group | I | II | III |
|-----------------------------------|-------------|-------------|----------------|
| Number of heats..... | 43 | 49 | 44 |
| Oxide range, per cent..... | 0.000-0.016 | 0.017-0.023 | 0.024 and over |
| Oxide average, per cent..... | 0.013 | 0.019 | 0.032 |
| FeO in slag, per cent..... | 11.9 | 12.2 | 12.5 |
| Seams and flaws, per cent..... | 3.2 | 3.6 | 3.5 |
| Drop-test ductility failures..... | 0.0 | 0.0 | 0.6 |

These heats are grouped according to the total silicon and manganese oxide content of the finished steel, and increasing percentages of oxides in the steel are associated with only slight increase in the ferrous oxide content of the slag, which indicates that the iron oxide in the slag is a less important factor in determining the oxides in the steel than other factors

in the furnace practice. These results also show that the oxides in the steel have only a minor effect on the seams and flaws present on the finished rails. The high-oxide group is definitely associated, however, with decreased ductility at the drop test.

The above considerations with respect to economy of production and quality of the finished rails have led to our establishing a range of 10 to 15 per cent ferrous oxide, as being the most desirable composition for rail-steel slags.

The problem of slag control in the basic open-hearth process begins with the limestone charge. The stone must be fairly free of fines, for if allowed to be present in any great quantity, sticking of the flux to the furnace bottom will lead to irregular and sometimes soft melts with the attendant high iron oxide content in both metal and slag. For best quality rails, we are not desirous that the ferrous oxide be more than 12.5 per cent in the slag at 0.25 to 0.30 per cent carbon, in order to finish with a maximum of 15 per cent when the bath is ready for the liquid recarburizer. In order to obtain a sufficiently high lime-silica ratio in the slag, and to attain adequate slag volume, the amount of stone put into the furnace, with a normal scrap and hot metal charge, must not be less than 9.5 per cent of the total metallic charge. For the same reason, if the silicon in the hot metal is running high, say over 1.30 per cent, or where the recarburizer amounts to 13 per cent instead of the usual 10 per cent, the initial stone charge is raised from 9.5 to 10 per cent.

The amount of limestone being fixed within these limits, the lime-silica ratio must be guarded, subsequently, through the selection of metals charged. The scrap must be free of skulls, wheels, rolls, and stove plate detinned, and carry a good proportion (30 per cent) of heavy melting material—preferably bloom scrap. The hot metal must range in silicon between 0.80 and 1.35 per cent and have a maximum phosphorus content for recarburizing purposes of not more than 0.180 per cent. The aim of all this initial procedure is to insure the attainment of a lime-silica ratio of at least 2.8 to 1 at 0.30 per cent carbon and one of 3.1 to 1 at 0.15 per cent carbon when the bath is ready for its metal recarburizer. This basicity has been found necessary to produce the best quality of rails. If these precautions are taken and the scrap and hot metal are proportioned approximately 44 to 56, the heat will melt where 3000 to 5000 lb. of ore is required to bring the bath down to recarburizing carbon.

Thus we can see that our original charge goes a long way in determining the slag composition we will have to work with in finishing the heat. The amount of stone lays the groundwork for the slag's basicity. Its freedom from fines influences not only the way the heat will melt, but also the amount of iron oxide that will be contained. With limits set on the stone we have shown that limits must, subsequently, be set on quality and quantity of both the scrap and hot metal charged, lest the objec-

tives in mind for what the limestone will give the slag be fundamentally disturbed.

The scrap should be melted down quickly in order to insure a prompt hot metal charge. Otherwise, irregular melts and high iron oxides result. If excessive ore is used, the lime-silica ratio is lowered and the iron oxide in the slag will also be forced downward. Under such conditions burnt lime must be added to build up the basicity and iron oxide content of the slag. The addition of spar will raise the FeO 1 to 1.5 per cent if the slag is inclined toward lumpiness. With the bath at 0.28 to 0.30 per cent carbon, the slag should be shaped well enough to warrant a determination of FeO content and thus give some idea of the extent to which it will function in handling the recarburizer when it is added, approximately two hours later. If excessive ore additions have been necessary, burnt lime is arbitrarily added at this point along with a batch of spiegeleisen. The FeO content at this stage should be 9 to 15 per cent. If it is lower than 9 per cent, the FeO is built up through the addition of more burnt lime. The slag should be quiet, and of a creamy consistency. At 0.15 per cent carbon, and after a second batch of spiegeleisen, the bath must be made ready for the recarburizer. The slag must be cooled down, and this procedure lowers its iron oxide content 1 to 1.5 per cent. Therefore it is preferable to have the slag close to 14 per cent FeO at this time.

The furnace practice thus shapes the slag for which the fundamental characteristics have been set by the initial charge. The addition of too much ore constitutes an excessive input of silicon, with the consequent loss of basicity and iron oxide in the slag, making necessary the use of a counteracting agent—burnt lime. The effectiveness of spar in building up the basicity and iron oxide, is, as we have shown, especially felt where the slag is lumpy.

The problem of controlling the many involved factors governing the composition of rail-steel slag may be summed up as one of the selection and balancing of the initial charge and the application of correctives in the working practice as quickly as variables appear. When consistently followed, slag control has proved its worth, as we have pointed out above, not only from the production standpoint but also with respect to furnishing a product that is more satisfactory in service.

DISCUSSION

R. H. SWEETSER.—I should like to ask whether the ore is heavy, lump, high specific gravity ore, or red hematite?

W. J. REAGAN.—We have a hematite lump ore to start with, but it is screened to recover the fines, as the fines remain in the slag. When both fines and lumps are added the fines remain in the slag and the lumps go into the bath. When fines only are used and the amount added, accurately weighed, it is possible to calculate the

amount of FeO that is being added to the slag in the form of fine iron ore. Roll scale will answer the same purpose.

R. H. SWEETSER.—That is very different from what has been done; previously a very high specific gravity iron ore was wanted, and wanted in lumps, so there must be some change in open-hearth practice if they are going to fine ore.

L. F. REINARTZ.—We are using a regular hematite ore. We do not use lump ore any more.

G. B. WATERHOUSE,* Cambridge, Mass.—That is a change in open-hearth practice. Won't some one tell us why they have changed; why they have swung over this way?

W. J. REAGAN.—I think some of the statements that have been made are somewhat misleading to Mr. Sweetser. We have not changed our practice in the use of iron ore. Our ore supply consists mostly of lump ore with the usual amount of fines. It is known commercially as "Cliff Shafts Lump Ore." This is the ore that is used for the reduction of carbon and is added in quite sizable amounts; in fact, I would say that 90 per cent or more of our ore consumption is of this type of ore. By screening this ore to remove all lumps we obtain a fine ore that is used to add iron oxide to our slag on heats where the iron oxide is deficient. There are a *great many heats* where this fine ore is not used at all. Because lump ore goes through the slag and into the bath it is necessary to use fine ore to have it remain in the slag. In the making of rimming steels, etc., I believe it would be advisable to use ore with a larger percentage of fines, as in the making of these steels a much higher iron oxide is carried in the slag. Probably this is the reason Mr. Reinartz is using an ore with a greater amount of fines in it.

A. L. FEILD.—Is lump ore or fine ore more effective in removing carbon; that is, for a given weight of ore, which lowers carbon more rapidly? It has been my experience that lump ore is more effective, because it gets right down on the metal bath.

W. J. REAGAN.—I agree with Mr. Feild's idea that lump ore is more efficient in removing carbon. However, if it were possible to get fine ore into the bath I believe that you would get a much greater reaction than would be possible with the lump ore. The particular reason for using the lump ore is that it goes through the slag and into the bath.

R. H. SWEETSER.—Well, I should like to ask this question: If you desire to get the ore down into the metal, why not use a high specific gravity iron ore, even if it is in small pieces? The fix ore, or the lump ore, as they have been calling it for open-hearth practice, has generally been demanded as a very high specific gravity iron ore, and the iron ore men have been told that they wanted it in lumps and they wanted it heavy so that it would get down into the bath. Now it seems you want something that will just float along in this bath of slag on top of the metal bath, and it was just for the sake of bringing out that point that I asked those questions. Now, for instance, would a very rich fine ore, say $\frac{1}{4}$ -in. stuff, of magnetite get down into the metal through the slag?

A. L. FEILD.—It seems to me that, if you are talking about slag control, and control of the iron oxide content of the slag, the fine ore which goes into solution in the

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slag enables you to make calculations, but when you put in lump ore you do not know whether to call it slag or not. You cannot attribute to it any effective percentage addition of iron oxide to the slag.

L. F. REINARTZ.—We are talking about two different uses of iron ore. Fine ore is used usually in low-carbon steels to regulate oxidation of the slag. If carbon must be reduced rapidly in a high-carbon steel bath, lump ore should be used. In low-carbon baths, it is more important to get the fine ore into the slag than to have lump ore react directly with the metal.

Slag Control for Alloy Forging Steel

BY A. L. FEILD,* MEMBER A.I.M.E.

This general subject has been so thoroughly discussed by Dr. Herty and his associates, especially with regard to the degree of oxidation of the metal at the time that the silicon pig or spiegel is added, that I am not going to spend much time on that today.

I should like to propound a question, which is based on my own observations made some years ago while with a large alloy-steel company which had two open-hearth furnace plants. It is true that one of these plants was not engaged particularly in making alloy steels, but there were certain relations between slag and metal composition which appeared to me to be entirely different in the two plants. I have an explanation for it that is more or less incomplete, but possibly Dr. Herty or Mr. Reinartz or some of the others may be able to complete it.

Suppose we take our three layers; the metal on the bottom, on top of that the slag, and on top of the slag, the gas. We cannot overlook the gaseous phase.

Regardless of the effect of the iron oxide in the slag on the rate of carbon elimination—and that, of course, is rather important in alloy practice since it is not desirable to have the carbon dropping too rapidly at the time the deoxidizing is had in the furnace—it will probably be admitted that it depends on the iron oxide in the metal for a given carbon oxide.

I have seen cases where with approximately identical metal and slag compositions one furnace would work twice as rapidly as another in removing carbon. Of course, there is some explanation of this in what others have already said, that the question of the exact lime and silica content of the slag determines the activity and viscosity of the slag; but I am convinced, without having reviewed the actual records since I was asked to make this talk, because they were not available at the time, that the slags in these two furnaces were not materially different. Putting it another way, one furnace would have

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taken a good deal longer to turn out a heat than the other if the same iron oxide content had been present in the slag in both cases. The result was that the slag in one set of furnaces consistently ran higher in iron oxide than the other. I thought at first it was a question of temperature, and it may have been connected with temperature, but in order to account for the difference in rate of carbon elimination by temperature alone it would have been necessary to assume that it was proportional to the fifth or sixth power of the temperature, which struck me as being rather fantastic.

I believe we all know that furnace builders and furnace operators differentiate between two types of open-hearth furnaces. I am speaking, of course, of basic open-hearth practice. Unfortunately, I have had practically no acid experience. There is such a furnace as a fast-working furnace, and there is a slow-working furnace, and the differences cannot be due, in my mind, to random variations in slag composition.

The question I would like to propose is this: Since the oxygen for the working of the heat comes from the furnace gases, the slag simply acting as a carrier, is it not possible that the way in which the flame strikes the slag, and flows along the surface of the slag, has a great deal to do with this problem of slag control?

As you know, the gas passing through an open-hearth furnace really flows upward against the roof. Being highly heated and low in density it rises, and the action here, unless the flame were directed uniformly toward the bath, would vary a great deal, depending on open-hearth design and rate of fuel consumption.

I am particularly anxious to get Dr. Herty's opinion on this matter because he is working on the subject at the present time. My excuse for discussing this under the heading of alloy practice is that when chrome-nickel or chrome steel is made in the basic open hearth there is nothing more important than the condition of the slag, not only because of its reaction with the metal but because of mechanical losses.

With the same iron oxide, lime and silica content, one of two furnaces sending its flame more nearly against the surface and along the surface of the bath, and possibly raising the temperature of the slag surface higher than normal, would probably behave entirely different from one in which the gas did not have this behavior. Experimental difficulties, of course, of measuring anything in the way of temperatures in a furnace, or even of measuring gas velocities, are very great.

Speaking broadly on the question of slag control, I think we should not pride ourselves too much on what has been done so far in the way of contriving expedients and theories for controlling slag and iron oxide, because if most of these are "boiled down," they resolve themselves into a more or less scientific explanation of what the uneducated or non-technical melter has always done. If it is concluded that slag control

goes back to lime in the charge and the silicon content of the pig iron, that has always been much discussed by the practical melter.

DISCUSSION

C. H. HERTY, JR.—I do not remember whether it was at an open-hearth meeting or at one of our metallurgical advisory meetings in Pittsburgh, we proposed the idea of looking at a furnace in a little different section. The general shape of the bath was oblong. We spoke of the bath as having so many square feet of slag-metal area or slag-gas area. What we were vitally interested in was the combination of area and activity; in other words, agitation that resulted in faster diffusion in a sharp-working furnace. We had an area of quite violent agitation, due to the impinging of the gas, resulting in a higher rate of transfer in this area; and there was a slow-working furnace which did not throw the gas down right. You had the same area, but it was much less active, therefore your iron oxide was transferred more slowly. I mean, that is particularly true with a furnace that is working fast in the middle of a campaign and an old furnace where the checker tends to be clogged. In other words, the slag may be exactly the same but the rate of transfer will be much slower, because there is not the same activity per square foot of slag as in a sharp-working furnace; and for that reason the various equations fail to take into account the fact that although 450 sq. ft. of slag-metal surface may be calculated, the real interest lies in the over-all activity per square foot, which cannot be measured simply by looking at the furnace; and we all simply say that a fast-working furnace transfers more iron oxide per second per square foot than a slow-working furnace does, meaning that the agitation is greater in the faster furnace.

It is just as Dr. Lewis used to tell to us at M.I.T. about humidifiers; that with a certain number of brushes to humidify the air, a certain degree of humidification would be obtained, but that if those brushes were rotated a tremendously greater degree of humidification would be obtained, simply because the area and the gas velocity past any given drop of water had been increased and therefore the rate of transfer had been increased.

I think the proposition that you put up is perfectly correct, that it is the function of something that we cannot measure. It just cannot be done, because we do not know enough about the exact agitation per square foot at any part of the bath, and we have to express it as the total over-all surface. You can go backwards, of course, and say that the faster the rate of carbon drop, the greater the agitation, and you can calculate it back and prove what you have said very nicely. You will not have done anything, however, except fill up a lot of paper and pages. But I think the proposition is perfectly true, that it is a question of agitation due to proper gas impingement more than anything else.

A. L. FIELD.—You speak of gas impingement on the surface of the slag and the effect in increasing slag activity. Where does the temperature come in? Is there not an increase in temperature also? What is the relative importance of temperature as against agitation?

C. H. HERTY, JR.—As a matter of fact, we do not know anything about temperature, when you come right down to it, except that manganese, phosphorus and silicon can go out fast at low temperature, or are supposed to go out faster at low temperatures, relatively, than the others, but it is common knowledge that if you get a heat very hot, you cannot drop carbon fast. Obviously, then, high temperature in that zone has nothing to do with it, if we accept that with a hot heat you can hold carbon. In other words, some of the new data on the iron oxide-carbon reaction makes uncertain the temperature effect on that reaction. But it is a fact that higher temperature

should make carbon drop faster on account of agitation, and if you want to hold a carbon, all you have to do is to get your heat hot enough.

A. L. FEILD.—While we cannot measure slag temperatures very well, what are the probable differences in slag temperatures in different furnaces? Of course, inadequate checkers was the explanation offered for those slow-working furnaces, but does modern practice involve much variation in the operating temperatures of basic open-hearth furnaces?

C. H. HERTY, JR.—Probably you remember the time studies we made in Lackawanna practice a long time ago, when we ran a number of heats at such slag temperatures, and the difference between a fast and a slow-working furnace in that particular test seemed to me to be about 125° difference in the average slag-surface temperature. Of course, the difference in the temperature between the upper and lower surface of the slag is something else. The Germans, I think, have found that an average of about 30° to 40° C.

Slag Control for Alloy Forging Steel

By R. C. GOOD,* MEMBER A.I.M.E.

Slag control for any kind of steel, rimming, straight carbon or alloy, should start with the charge and be developed well in advance of the tap because its composition, viscosity and temperature will unquestionably govern the physical and chemical properties of the steel when tapped.

In the majority of plants producing alloy steels, primary consideration is given to the chemical specifications; physical characteristics usually occupy secondary place in the melter's mind. Recently, however, buyers have indicated limits of machinability, hardenability, grain size and, of course, always wanted steel free from foreign nonmetallic inclusions. It is these latter specifications that require the attention of the operator to the slag and its control.

The slag must act as a vehicle for oxidized elements originating from the metallic portion of the charge; it should hold the oxides of phosphorus, silicon, manganese, iron and chromium that come into contact with it either before or after the refining and finishing stage of the heat. It must be used as a transferring medium of oxygen from the atmosphere or oxide additions to the metal and should permit a free escape of gas generated within the charge. Finally, the slag is the principal controlling factor in regulating the rate of oxidation which in turn eventually determines the quality of the steel as measured for the various characteristics mentioned above.

With pig iron of uniform composition, the iron oxide in the slag increases as the limestone is increased but with the same addition of stone in every heat, the iron oxide decreases as the silicon is increased in the charge, and vice versa.

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Careful weighing or estimating of the limestone charge for the furnace is not unusual; selection of scrap with respect to nonferrous and oxidized metal may be given very close attention, but the pig iron or hot metal is bought or made without sufficient consideration for its influence on the quality of the steel. Iron containing 1.10 per cent silicon may be perfect from the viewpoint of melting and refining providing the silicon is not present as SiO_2 and exceptionally fine steel may result, yet two days later the iron may contain 1.35 per cent silicon or 0.90 per cent silicon and the open-hearth department is supposed to duplicate the quality obtained on the first heat.

We are told by the open-hearth superintendents that they followed exactly the same procedure, used silicomanganese in the furnace and specified alloys in the ladle. It is believed that a comparative analysis of the log sheets from a series of heats treated with silicomanganese will verify a simple but important fact. In a majority of cases checked by the speaker it was learned that the use of silicomanganese is not sufficient for the best results, and the cleanest steel was obtained when the manganese loss exceeded the silicon loss by at least 50 per cent. That is, from the killing of the bath to the pouring of the ingot you should oxidize at least twice as much manganese as silicon if the steel is tapped before the bath opens up again.

You will appreciate the reason for this requirement by giving some thought to the general theory. Through economic pressure we use silicon to stabilize the carbon, which in the next 10 to 20 minutes is converted to SiO_2 . In order to flux the SiO_2 enough MnO is necessary to form a natural silicate of these two oxides with a low melting point and strong tendency to rise, and as the atomic weights of manganese and silicon are as two to one we must oxidize twice as much manganese as silicon.

Just how this plan is to be accomplished may vary considerably from plant to plant, but several pertinent facts may be noted. Silicon loss will depend mainly on the degree of oxidation of the bath at the time of the addition, which in turn depends principally on the iron oxide in the slag and its physical condition. Manganese loss depends also on this condition plus the temperature of the metal, the fluidity of the slag and the length of time the steel remains in the furnace after the deoxidizing addition and before tapping.

Ordinarily, a definite amount of, say, silicomanganese is added to the bath, depending on final chemical specifications and the iron oxide in the slag at the time of the addition. Ten to 25 minutes later either more manganese as ferromanganese or ferrochrome is added to meet specifications. During the interval before tapping manganese silicate formed will rise and dissolve in the slag, providing the slag is not too cold, whereas SiO_2 alone may not. The percentage of MnO in the slag apparently has no influence on the rate of manganese oxidation.

Slag Control in Acid Open-hearth Steel

By FRANCIS B. FOLEY,* MEMBER A.I.M.E.

Fundamentally, slag control in acid open-hearth steelmaking cannot be considered from any different viewpoint than can that in basic open-hearth melting. The same laws of mass action and distribution apply in both cases, so that while most, if not all, of the recent intensive study of slag-metal reactions have been carried on in basic furnaces the principles evolved are nevertheless applicable to acid open-hearth steelmaking and it is therefore not our intention to discuss the various possible chemical reactions in the slag and between slag and metal. The points we have to carry in mind, in considering acid melting practice, are the differences in the type of steels produced and the difference in the chemistry of both the steel and the slag.

The acid furnace is used to produce, let us not say "quality" steel, for, after all, a "quality" steel for one purpose is not a "quality" steel for another, but steels that require acid melting practice to be of proper "quality." Steels that are required to have high physical properties in tests taken transversely from forgings are peculiarly the product of acid furnaces. In this class may be placed various ordnance materials, notably gun forgings and projectiles and large commercial forgings requiring high transverse ductility. Forgings requiring an extremely hard surface, polished and free from imperfections, are also typical acid-steel products. Of course, such forgings can be made of basic open-hearth steel, but not with the same assurance of success.

At the start, the preparation of the slag in the acid and basic furnaces differs. Lime is charged in the beginning of a basic heat to form a slag, but in the acid furnace nothing is added for the special purpose of producing a slag when the heat is melted down. The result is that the acid furnace has much less volume of slag than the basic. The slag formed upon melting down is made up almost entirely of the oxides of elements contained in the metallic charge, notably oxides of iron, manganese and silicon, the amount of silica being augmented somewhat by erosion of the furnace lining.

A typical acid open-hearth slag, when the bath is completely melted, will have an analysis about as follows: CaO , 3.40 per cent; SiO_2 , 51.9; Fe_2O_3 , 1.25; FeO , 28.86; Al_2O_3 , 1.82; MnO , 12.22.

The high iron oxide content of the slag gives it a black appearance. The metal is high in carbon and some manganese and silicon will be present, depending on the amount in the original charge, the amount of

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these elements present in the charge governing, to some extent, the FeO content of the slag that is formed. The slag being high in iron oxide, the bath high in carbon and the furnace temperature rising, there is a normal reduction of the iron oxide by the carbon in the bath. In this manner the carbon content of the metal is reduced and the slag clears up as its iron oxide content is lowered, its color changing from black to brown, to yellow and, finally, to a light color, the tint of which is affected by the amount of manganese oxide present. The speed at which this change takes place depends on the operation of the furnace and the maintenance of a proper balance of the air-fuel ratio to avoid, on the one hand, conditions that are too oxidizing and, on the other hand, loss of temperature.

Since the addition of some ore is desirable it is necessary thus to clean up the slag so as to be able, during the oreing period, to estimate the proper rate at which to add the ore. It may be desirable to hasten the conditioning of the slag by adding carbon in the form of coal to reduce its iron oxide content. In order to maintain a slag of the proper physical characteristics, some limestone is also added. The slag having been gotten into condition, additions of ore are made to bring the carbon content to the desired point. With proper attention to the slag, such ore additions should not increase its iron oxide content and, when the heat is ready to go ahead, its carbon being at the desired point, silicon is reduced from the slag, causing a pickup of silicon by the bath. The result of this reduction of silica is not more than a momentary reduction in the silica content of the slag which, due to some erosion of the hearth of the furnace, steadily increases up to the end of the heat. An addition of ferrosilicon is made at this point in the heat to hold the carbon. This is the end point in the conditioning of the slag. At this point the slag composition will have changed to: CaO, 8.2 per cent; SiO₂, 60.95; FeO, 13.64; Al₂O₃, 2.15; MnO, 12.76.

TABLE 5.—*Slag Determinations on Random Heat of Carbon Steel*

| Time | Slag, Per Cent | | | | | | Metal, Per Cent | | |
|------------------------|----------------|------------------|-------|--------------------------------|-------|------|-----------------|------|-------|
| | CaO | SiO ₂ | FeO | Al ₂ O ₃ | MnO | MgO | C | Mn | Si |
| 10:40 a.m. melted..... | 3.40 | 51.90 | 28.86 | 1.82 | 12.22 | 1.65 | 1.34 | 0.73 | 0.275 |
| 10:55-12:30 added ore. | | | | | | | | | |
| 12:30 added lime..... | | | | | | | | | |
| 1:00 p.m..... | 5.30 | 58.70 | 19.40 | 2.08 | 12.50 | 1.72 | | | |
| 1:30 p.m..... | 8.20 | 60.95 | 13.64 | 2.15 | 12.76 | 1.80 | 0.65 | 0.07 | 0.02 |
| 2:00 p.m..... | | | | | | | 0.56 | 0.07 | 0.02 |
| Added Mn and Si... | | | | | | | | 0.80 | 0.16 |
| 2:40 p.m..... | 9.10 | 61.16 | 12.43 | 2.25 | 13.00 | 1.85 | | | |
| Final analysis..... | | | | | | | 0.57 | 0.73 | 0.25 |

It is not necessary to determine the silicon content of the metal to find out when the end point in condition has been reached, but the experienced acid open-hearth melter in pouring tests readily recognizes the end point by the manner in which a test settles in freezing. He has already noted its approach from his slag characteristics, both in the furnace where it lies flat and motionless and from its light color.

From the time of making the ferrosilicon addition to tapping the heat, changes in the slag composition are of a minor character and arise from whatever oxidation may chance to occur of the final additions made to the heat to produce the desired chemical analysis.

Table 5 shows a series of slag determinations on a random heat of carbon steel.

DISCUSSION

R. C. GOOD.—In the past 10 or 15 years, perhaps, the question as to whether reduced silicon from an acid slag is beneficial or otherwise has been a controversial issue, and in acid electric-furnace practice it has been found to be detrimental. How does Mr. Foley account for the fact that in his acid open-hearth practice it must be beneficial or they would not use that practice?

F. B. FOLEY.—The acid open-hearth melter does not aim to obtain a silicon pickup for the sake of the increased silicon. The silicon pickup happens to be a good indicator of an end point. It is a point in the conditioning of the slag and the operation of the furnace which the metallurgist recognizes.

It is not the amount of silicon reduced that is important. In days gone by some melters carried the reduction of silicon on to a much further extent than they do today, but, in modern practice there is not sufficient silicon picked up by the heat to be detrimental. We know that in making electric-furnace steel residual silicon has not the same effect as added silicon and, no doubt, the same thing may apply in acid open-hearth practice. A silicon pickup of 0.10 per cent has not been found to be a detriment in acid-steel practice. It has been the experience, as you say, in electric-furnace operation that silicon carried through a heat does no good and, as a matter of fact, has been found to be bad.

Slag Control for Basic Electric-furnace Steel

By HARRY F. WALTHER*

Basic electric-arc furnace steel production mainly involves the use of two separate types of slags. The first, known as the "melt down" or oxidizing slag, which is in most cases removed from the furnace mechanically, and the heat finished under the second or deoxidizing slag, which is commonly known as the "finishing slag."

The melt down slag is formed by the addition of lime or limestone to the charge, which combines with the oxides formed during the melting period and the product of any bottom erosion that may take place.

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Under ordinary conditions this slag will be of the high-lime type and slightly oxidizing. The oxidation of phosphorus and silicon takes place in this slag; also some carbon and manganese are eliminated along with any other element of an oxidizable nature that may exist in the charge. The reduction of these elements is dependent upon the degree of oxidation which is easily controlled. In some special cases the charges are melted without any oxidation, where it has been found practical to melt selected scrap in such a manner so as to conserve the residual alloys.

There are several types of finishing slags in use in making the various steels. The lime-silicon slag is used widely in the making of the low-carbon steels, which include the stainless types. This method of slag-making has been found satisfactory where the possibility of carbon absorption due to the use of carbon in the slag as a reducing agent would constitute a melting hazard. The lime-aluminum slag is used to some extent, where aluminum borings are available at a low cost. In forming this type of slag it is necessary to use lime of a very low silica content, since aluminum is a very powerful deoxidizer, and easily reduces any silica in the slag. The lime-silica slag is used on some steels to impart some definite physical characteristic to the resultant product. In producing steel with this type of slag no deoxidizer is added to the slag, the value of the slag being dependent upon a fixed lime to silica ratio. There are several other methods of forming slags with special compounds for which merit has been claimed.

Most of the electric-furnace steel of the engineering grades is made with the calcium carbide slag as the finishing slag. When properly handled it is a powerful deoxidizer and can be so controlled that the chemical composition of the bath can be held within very close limits. It is also one of the deciding factors in the control of inherent grain size, which has become a metallurgical requirement in most steels.

Obviously, if consistent results are to be obtained it is absolutely necessary to systematize the melting procedure from the buying of the raw materials to the delivery of the finished ingot. The day of haphazard melting has disappeared and in its stead is found the production of steel of superior quality with consistent characteristics, which is possible in the electric furnace.

When a heat of 0.50 per cent carbon steel is ready to be slagged off, the slag will analyze approximately as follows: calcium oxide, 48.78 per cent; silica, 23.40; ferrous oxide, 8.93; manganese oxide, 5.26; magnesium oxide, 7.10; ferric oxide, 1.92; phosphoric acid, 0.24; alumina, 1.50; sulfur, 0.17; calcium fluoride, 1.20. This typical oxidizing slag compares closely to an open-hearth slag.

If the slag is slightly foamy and the bath is reacting lightly, it is a true indication that the charge is completely melted, and the bath is in proper condition to be deoxidized. The initial slag requires from 40 to

50 lb. per ton of limestone in the charge, or its equivalent in burned lime. Care must be taken that the temperature of the bath is correct and the slag is in proper shape at the completion of the melt. Ease of control of the heat is dependent upon the condition of the bath at the slagging-off period. The oxidizing slag should be removed from the furnace as cleanly as possible, since the objectionable phosphoric acid would be easily reduced in the following slag.

The success of efficient slag control during the deoxidizing or finishing period depends upon the following seven factors: (1) moisture-free materials; (2) consistent chemical and physical characteristics of the materials; (3) correct temperature of the bath; (4) quick fluxing action; (5) proper slag volume and mix; (6) power input; (7) time, and (8) bottom upkeep.

The hydrogen set free by materials containing moisture is easily absorbed by the hot metal. Chromium steels are particularly vulnerable when silicon is present and if hydrogen is present in any appreciable amount will cause porosity in the top section of the ingot as it is released during solidification. Since little is known as to the elimination of this gas in the furnace, the obvious procedure is to keep all hydrogen-forming compounds out of the furnace.

The lime, sand, fluorspar, coke or any of the fluxes in common use must be constantly checked if consistently uniform slags are to be made.

The bath temperature must be closely controlled, since varied temperatures during melting and pouring of a particular type of steel impart somewhat different characteristics to the slag and the finished product.

Finishing slags should be designed to flux quickly. The mixture is dependent mainly on the type of burned lime available, since its composition varies greatly and reacts with varying results in the furnace. When grades of slag-forming materials have been decided upon, it will be advantageous to mix them in their proper proportions and charge into the furnace after slagging off. Some carbon in the form of crushed coke or crushed electrode can be added to this mix in the higher carbon steels, but is not advisable for low-carbon types. Enough coke should be spread on this mix to form calcium carbide and establish deoxidation, and to insure that hot carbon monoxide gas is produced in sufficient quantity to build up a positive, or outward, pressure. This prevents excess air from entering the furnace and maintains the furnace atmosphere and slag in as perfect a reducing state as possible. To facilitate this condition it is essential, of course, that the furnace be sealed as tightly as possible and that there be no water leaks.

Practical considerations play an important part in determining the proper slag volume. It must be of sufficient volume and viscous enough to prevent excess coke from coming in contact with the molten metal, thus assuring close carbon control. There must be enough slag present

to prevent the arc from contacting the metal directly, as the reactance on the slag is less, when of the proper composition, than on the metal, thereby permitting a smooth and steady power input. And finally, there must be enough slag to conserve the temperature of the metal in the ladle to the end of the pour.

Maintaining the delicate electrical equipment of the modern high-powered furnace is absolutely essential to efficient operation and slag manipulation in the hands of a skilled operator.

Slags, when efficiently made, should be in a nearly perfect condition 45 minutes after slagging off (Table 6). It is evident that no real constitutional difference existed between the time the first slag sample was taken and one hour later when the heat was ready to tap. From the analyses both slags are indicative of being in a highly deoxidized state. While calcium carbide is a strong deoxidizer, it remains for silicon and aluminum to completely degasify the metal to produce sound ingots, the use of which, however, can be held to a minimum.

TABLE 6.—*Effect of Time on Finishing Slag*

| | Chemical Composition, Per Cent | |
|-----------------------|--------------------------------|--------------------------------|
| | 45 Min. after Slag Off | 1 Hr. 45 Min after Slag Off |
| Carbon | 0.53 | 0.77 |
| Calcium carbide..... | 3.68 | 2.54 |
| Calcium fluoride..... | 5.90 | 2.80 |
| Calcium oxide..... | 57.84 | 60.62 |
| Silica..... | 21.86 | 24.54 |
| Chromic oxide..... | 0.05 | 0.03 |
| Alumina..... | 2.76 | 3.08 |
| Ferrous oxide..... | 0.43 | 0.29 |
| Ferric oxide..... | nil | nil |
| Manganese oxide | 0.17 | 0.09 |
| Magnesium oxide..... | 4.96 | 4.24 |
| Phosphoric acid..... | 0.06 | 0.07 |
| Sulfur..... | 0.36 | 0.36 |

Since the slag is practically free from all metallic oxides, it is obvious that subsequent additions of ferroalloys cannot be oxidized in this type of slag and will go into the bath without loss. Since completely deoxidized steel can be made in the furnace without resorting to ladle additions, it is evident that clean steel can be made by efficient furnace operation and slag control.

Considerable attention must be given to the materials used in the bottom and lining of the furnace, since erosion is an ever present problem, the results of which are readily reflected in the slag and quality of the steel.

Since the inception of the 40-hr. week it has become of increased importance that a definite method of procedure be followed and that practices be standardized to eliminate the human variable as much as possible.

The question often arises as to whether the slags can be controlled as easily in the 100-ton furnace as in the smaller furnaces. The correct answer is yes. Experience has taught that standardization is increasingly important with the increase in furnace capacity, and if followed judiciously will result in the production of steel of superior quality with the melting hazard at a minimum.

DISCUSSION

F. T. SISCO,* New York, N. Y.—What is the practice if the carbon is a little too high before the heat is tapped? Is the white slag removed and the heat ored down or is the high-carbon steel tapped and used as scrap?

H. F. WALTHER.—If you are going to oxidize the heat after it is ready to tap, you might as well scrap it. However, it is possible to have low-carbon scrap sufficiently clean to add to the furnace while the carbide slag is still on the heat, and absolutely not set up any oxidation whatever; simply lower the carbon or any element that has gone beyond control by dilution. This method works out well in the higher carbon steels. In low-carbon steels, it is best to change the type or scrap the heat.

F. T. SISCO.—There is another thing. On your 100-ton furnace, how many heats do you usually get on the roof and walls?

H. F. WALTHER.—Our cost per ton is a great deal less on a 100-ton furnace than on any other type of furnace we have, and our records will show that we are getting in the neighborhood of 40 heats on our roof, and we have had as high as 74 on a lining, which is excellent for that type of furnace. The average runs around 60 right now on the lining. However, I might say this, that quite often the lining is worth a few more heats, but when the roof has become thin, it must be changed. Temperature is being lost anyway, owing to the change, and it really does not cost much more to tear the furnace down and reline it quickly, and go right ahead with a brand new furnace. Thus eliminating one expensive shutdown and tonnage loss.

C. D. KING.—Mr. Walther spoke of these heats working equally well in a 100-ton furnace. Is that predicated on the same hearth areas per ton of ingots, or do you proportion your large furnace to give you extremely large area to take care of it, but smaller hearth area per ton of ingots?

H. F. WALTHER.—The 100-ton furnace has a very large area. The furnace shell itself is close to 20 ft. wide (19.6, to be exact) and 29 ft. long and elliptical in shape, and the depth of the bath runs around 26 in. Of course, bath depth varies in any furnace, regardless of the steelmaking, open-hearth or electric. It might at one time be 26 in.; the next time it may be 22, according to the depth in which the heat lies in the furnace; but if it lies 2 or 3 in. below the sill, the depth of that metal will probably be about 26 or 24 in., depending on the amount charged, and condition of banks and bottom.

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C. D. KING.—Perhaps I did not make my question clear. Assuming that there is 4 sq. ft. of hearth area for a ton of ingots on a small furnace, will you allow for a similar hearth area in a large furnace?

H. F. WALTHER.—The area will be somewhat less per ton. The bath is quite a bit deeper, necessarily so. A 1-ton furnace depth of bath would be about 6 or 7 in.; up to a 10-ton furnace it may run 16 or 18 in. In a 30-ton furnace that depth will be about the same as a 100-ton furnace, around 24 to 26 in. in the middle.

S. EPSTEIN,* Columbus, Ohio.—Have you noticed any relation between the condition of the slag or any factor in the working of the furnace and the tendency of the steel to flake?

H. F. WALTHER.—I am not sure that I can answer that question for you. Have we got any information along that line, Mr. Soler?

G. SOLER,† Canton, Ohio.—I do not believe we have. There seems to be no connection between the condition of the slag and the amount of flakes that might occur.

H. F. WALTHER.—Did you say furnace or slag?

S. EPSTEIN.—I mean the condition of the slag. Does the condition of the slag or the gassing of the steel, or anything like that bear any relation to the tendency of the steel to show flake?

H. F. WALTHER.—There is one thing we must take into consideration. We might know something about slags, may know something about temperature and size of furnaces, but just how much we know about the gases in the steel itself in the molten state, is hard to say. I pointed out that in our minds hydrogen exerts a very bad influence on steel, and the production of that hydrogen, owing to differences in handling slags, we can account for. Whether we have definitely gone on record as saying what slight difference might occur in carbide slags, I do not believe I could answer, because they are so uniform there really is not much difference in the slags themselves; their FeO content is usually way down, Fe_2O_3 is practically nil; in fact, we have the most perfect deoxidizing condition in the furnace itself. I cannot answer your question more definitely than that. Probably after we do some more work on the carbide slags we may have more information.

G. B. WATERHOUSE,—Mr. Epstein, do you know of any different relation between those?

S. EPSTEIN.—There might possibly be a relation, because according to the work Sims has done it would seem that steel castings with very low iron oxide content tend to show low ductility. Of course flake is caused by low ductility, not at room temperature, but at elevated temperatures. But still in your basic electric steel the iron oxide content is very low. I thought that sometimes you might get a steel with a higher oxide content, and that such steel might show less tendency to flake.

H. F. WALTHER.—I can say this much along that line, that some work has been done by allowing heats of steel to go through a very well reduced state of atmosphere and slag; that is, the carbide being very strong, which is around 2.5 to 3.5 per cent, allowing them to taper off, which simply means the allowing of air to come into the furnace to cause the FeO content to be somewhat higher in the slag. We find that this naturally can be done with low-carbon steels more satisfactorily than on high-

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carbon, and to produce that condition in high-carbon steel it is difficult to deoxidize properly and still try to tap with some oxygen in the slag. But we have done some work along that line, and the results, with a small amount of FeO in the slag, have been quite satisfactory. Flake is not a problem with us in tapping with low FeO in the slag. Steel made with carbide type slags with over 2 per cent FeO have not proved as good on micro, macro or grain-size ratings, or their control. I think flaking is tied up to some other phase of melting rather than to slight variables in FeO content of the slag.

R. C. GOOD.—I know that Mr. Walther is an excellent furnaceman, and I know that he uses sand in his finishing slag because it makes a nicer slag, but I should like to know whether he has any fundamental theory for the preference of sand over fluorspar, any technical reason for that?

H. F. WALTHER.—The type of slag we are after is one that will give reducing action as quickly as possible, and in experimenting with the ratios of CaO to SiO₂ we have taken them from 4 to 1 down to 1.5 to 1 lime to silica, and as far as reduction is concerned, it really does not make much difference, as long as the slag fluxes readily. The quick fluxing slag, at about 2.5 to 1, with a little fluorspar present, is the easiest and quickest fluxing slag we can form. Obviously, there must be enough silica in the slag to flux it properly. Some people use ferrosilicon, which I think is questionable practice. I really believe the production of stainless steel with the use of silicon in the slag has probably caused as much harm as it has good in reducing the slag.

C. D. KING.—You have made quite a jump from a 30-ton furnace to a 100-ton furnace. Do you see any material objection to a 200-ton electric furnace? Would it be practicable?

H. F. WALTHER.—Obviously, a 200-ton furnace would be a multiple-phase furnace. I do not know how many electrodes that would take. The electric furnace is not going to get any larger, as I see it now. We are handicapped, in the first place, by the equipment to use on the furnace, mainly electrodes. At present, an 18-in. electrode is the largest satisfactory electrode that the manufacturers can make. I can only hazard a guess as to a 200-ton furnace, of course, but I do not see how it would be practical. With a larger electric furnace it probably would be necessary to build a preheater and use oil or other fuel to keep the bottom hot to patch the furnace itself. A furnace of that size would be handicapped by a hole in the bottom. Obviously, when there is no input of heat once the metal has been tapped out, and if there happens to be a hole, that metal will freeze; and how can it be gotten out if it does not drain?

So, as the size of furnaces increases the troubles with maintenance of bottoms will also increase. I do not see how a 200-ton furnace could be over 19 ft. wide; it would probably have to be about 40 ft. long, and would have to be a furnace of the elliptical or oblong type. The shaping and changing of the roof would also present a great problem. I think it is beyond human control as yet.

A. D. PORTS,* Lockport, N. Y.—During a meeting at Pittsburgh last June, Mr. Gus Kayes, of the International Nickel Co., and Mr. Joe Scott discussed calcium and calcium reduction in steel. Of course they are interested in it because they are melting nickel alloys, and calcium is particularly detrimental to some types of nickel alloys.

We found that in using a lime fluorspar slag we got a reduction of both calcium and magnesium when the bottom came up in most any type of high-carbon steel. To lock the calcium and magnesium up, we went over to a lime-silica slag, and I think

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we had better forgeability in the steel with the lime-silica slag than we had with the lime-fluorspar slag. We have also found that the impact properties in the steel, when the heat has been melted under a more acid slag, are higher than those heats melted under a basic slag.

H. F. WALTHER.—At least you get quick fluxing action. That is the point I stressed, too. I can see no reason why a furnace should just set there. Since you want to deoxidize, why not do it as quickly as possible; and I think that type of slag you are talking about will do that.

You raised the point of calcium. I wonder if there is anybody here who knows what calcium looks like in a piece of steel or whether it is absolutely present. I think that question should be brought up. I have heard it discussed that calcium is being reduced, and that in the metal itself it is a harmful element; so far as we are concerned, we have not been able to discover calcium in steel. However, there are several persons propounding that, and if anybody has something to say about it, I am sure we would like to hear it, and whether the discussion concerns ferrous or nonferrous metals.

W. B. ARNESS,* Baltimore, Md.—I was pleased that Mr. Walther stressed the problem of hydrogen absorption by certain alloy steels. Particularly steels containing one or more of the elements silicon, nickel or chromium are susceptible, and as Mr. Walther points out, it is important to provide dry slagmaking materials.

However, control of hydrogen absorption may also be partially governed by slag manipulation. It is even probable that different furnaces or different melting practices will require different and special methods of slag manipulation.

On another subject Mr. Walther suggested that the arc-furnace charge should be hot when melted. This is usually desired, and a cycle of operation can ordinarily be worked out to accomplish it. But, I wonder if a radical change toward higher power input and consequent quicker melting might not increase seriously the difficulties of controlling the condition and temperature of the bath when melted. Most of us are limited in our experiences to some particular range of operating conditions; furnace capacity, power input, voltage, type of scrap, etc., and therefore an expression from Mr. Walther on this point would be appreciated.

H. F. WALTHER.—Possibly I am like you, I am wondering, too. There are a number of furnaces with as many as six and seven transformer taps, I believe, and the operator has to almost be a piano player to operate his furnace. We have found that three transformer taps are sufficient. One voltage at 120, one at the second tap or intermediate, 170, and the high at 195, have given us very good results on the 30-ton furnace, and I see no need for any more.

But your question of fast melting has yet to be worked out metallurgically. It is simply a question now of electrical apparatus, and if it means anything we can prove it only by the use of it. We are only hazarding a guess now. But I also stated that a heat should be slightly oxidizing at melt, and if we want to oxidize silicon, or a certain amount of carbon, by melting fast with no oxidation at all, we will still have to oxidize a little after we have melted. Erosion of the furnace is also a problem.

W. B. ARNESS.—Perhaps my question was not clear. For instance, I have seen a small furnace operated to melt so fast that the tendency of the electrodes was to melt from the top. In that case the electrodes never bored down through the charge in the accustomed manner, but tended to form a bath over the top of the solid charge. This type of practice introduces special problems, and I wonder if they have been studied in relation to large-scale operation.

* Melting Superintendent, Rustless Iron Corporation of America.

H. F. WALTHER.—What type furnace did you use?

W. B. ARNESS.—Just a small arc furnace.

H. F. WALTHER.—An electric-furnace charge melted from the top down?

W. B. ARNESS.—Yes.

H. F. WALTHER.—The scrap was not charged properly, or else it was too heavy and compact; or possibly the voltage was too high. Obviously, there must be enough light material on top of the heavy scrap used to permit the electrode in its melting function to bore down through to the heavy scrap in the bottom, where it starts forming the pool and comes back up. Obviously, you cannot melt from the top down. The length of the arc determines that, mainly. If the arc is so long at high voltage that it is melting over a wide area on the surface, it is going to melt from the top down with a consequential cold bottom. With a lower voltage at high amperage there is a good, strong arc, a hot arc, but not spread out so far. Consequently, it will bore through the scrap. That is the reason we have to put heavy scrap on the bottom and finish the charge with light on top. If you reverse that problem, that is, if you put the light scrap on the bottom and heavy on the top, the electrode will arc on the heavy scrap on the top, and the scrap, being heavy and compact, will take longer to melt, and may run out the doors on melting. Heavy, compact charges are very difficult to melt properly, especially with high voltage. Whatever the possible power input, it must be handled so that the charges are melted without skulling on the bottom.

W. B. ARNESS.—Of course, the operation that I speak of was somewhat of an extreme case, and was cited merely as an illustration. The usual melting-down problems are fairly well understood, but standard methods often do not apply to radically changed conditions. What I had hoped for was some discussion of the general subject of relation of high power input, high voltage, etc. to methods for controlling melting conditions.

H. F. WALTHER.—I think what started this discussion has not been answered yet. Mr. Arness raised the question of calcium. Has anyone anything to offer?

G. B. WATERHOUSE.—Have you anything on that, Dr. Kinzel? Have you found calcium in the steel?

A. B. KINZEL.—To the best of my knowledge, calcium as such has never been found in solid steel, and the solubility diagrams indicate that the amount that may be held in solid steel is extremely small. However, a calcium-silicon alloy has been used for steel deoxidation, not only for experimental work but also in regular production. This deoxidizer gives the desired deoxidizing results, and no attendant undesirable phenomena have been noted.

H. F. WALTHER.—We cannot prove that point, either, yet. Some people say they have.

A. D. POTTS.—You gentlemen probably have not worked with alloys that are susceptible to calcium or calcium carbide embrittlement, but there are certain iron-nickel alloys, iron-nickel chromium alloys, which if made under a slag that contains calcium carbide are almost impossible to work. If made under a lime-silica slag they can be worked out like a good piece of 10 carbon steel.

J. H. NEAD,* East Chicago, Ind.—Mr. Walther, how many electrodes do you use on the 100-ton furnaces, and do you use graphite or carbon electrodes?

H. F. WALTHER.—We use six, two separate transformers. The furnace can be operated from either end, but not efficiently. Both have to operate together. The electrodes are 18-in. units and are of graphite.

Physical Testing of Slag

By A. B. KINZEL,† MEMBER A.I.M.E.

Advance in the art of slag control has been very rapid in the past few years. The viscosimeter method for slag-reaction rate and composition, together with the phosphorus and other methods mentioned by Dr. Herty, allow the steelmaker to rectify and control the slag in the finish period of the heat with much greater precision than ever before. However, the steelmaker's problem is more complex, and in order to make steel of proper analysis in the most economical manner the constitution of the initial slag that has formed immediately after the lime is up in the furnace is of prime importance, as it is one of the factors that determine the carbon content of the charge as melted. Many heats melt with high carbon and some with carbon much lower than is expected so that, on the average, increased furnace time is necessary before reaching the finishing period. The problem, therefore, is to so regulate the slag-making additions that a suitable initial slag will be formed at once. Where all cold metal charges are involved, particularly where the iron and scrap are selected, this may be done with a fair degree of regularity. This regularity results not only in better conditions at the beginning of the heat and during the carbon drop, but also the need for smaller slag-modifying additions toward the end of the heat. The above has been well demonstrated by the work reported by Reagan in the past few years. Where large amounts of cold pig or hot metal are used, the problem becomes more involved. It is much more difficult for the steelmaker to be sure that for any given furnace the heat will form the desired initial slag. Observations of many heats indicate that the pig iron is a dominating factor in the constitution of the slag formed. The scrap is also a factor but in general could be roughly classified and a correction made therefor.

The necessity, therefore, arises for a method of correlating the pig-iron charge and type of slag formed for any particular furnace, which resolves itself into a measure of those qualities of the pig iron which affect the slag. The amount of silicon, manganese, phosphorus and sulfur in the pig iron will probably have some effect on the type of slag formed, but

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within minor variations. Simple analysis does not seem to be a controlling factor. However, certain analyses of pig iron are less sensitive to other factors, particularly the high-manganese pig. It has been observed that variation in initial slag and initial carbon on the melt down over an appreciable period is very much less with 2 per cent manganese pig than with the usual manganese content.

As the simple analysis of the pig iron is not the dominating factor, we must look further. It is well known that pig irons of normal analysis give trouble in bessemerization, whereas other lots of identical analyses are entirely satisfactory. It would seem that the oxygen-containing compounds in the pig iron were responsible for this phenomenon and that likewise these oxygen-containing constituents of the pig iron are responsible for the variation in the constitution of the initial slag and the carbon on initial melting. These oxygen-containing constituents comprise silica, silicates, iron and manganese oxides, and the various complex constituents formed with the above sulfides. It would further appear that the logical method of attacking this problem is to determine the amount and distribution of the oxygen-containing constituents. This could be carried out by means of the iodine method and the time necessary to do this is ample, as the sample for analysis could be taken at the blast furnace or mixer. In this way it would be possible to detect not only the unusually and obviously off iron but also iron that is not truly suitable for open-hearth use, which would not necessarily be classified as off iron under the present method. With such information available before the iron is actually charged into the open-hearth furnace, suitable adjustments in the amount of iron charged could be made.

It is generally recognized that different open-hearth furnaces will produce different types of slag, and in any given shop the oxide tolerants for each furnace would have to be determined in a manner similar to that now regularly used in the ratio of pig and ore added in the charge.

A good deal of experimentation and laborious correlation will be necessary before these suggestions can be brought to a stage where they can be applied in practice. However, only the most elementary arithmetic is necessary to indicate the possible savings to be effected by the solution of this problem. Said savings are indicated not only in the furnace time but also in the rolling.

GENERAL DISCUSSION

R. B. SOSMAN,* Kearny, N. J.—Mr. Sweetser brought out that in certain blast-furnace slag compositions a change of one or two tenths of a per cent may be quite significant. That is true not only of blast-furnace slags but of other compositions as well. We have all been up against the necessity of having to plot out equilibrium diagrams of this kind on a big enough scale so that we could actually use them, the

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small diagrams published in the journals being entirely too small for use. It is a good deal of a task and when one is through there is only one copy.

We thought that we would replot some of these diagrams, using the latest available temperatures and compositions, bring them up to date, and then reproduce the copies for general use. The difficult part of the job, of course, is the reproduction. We therefore took the problem to one of the best mapmakers in the country, outside of the Federal mapmaking services; namely, Williams and Heintz, of Washington.

Heretofore we have had to fall back on the Germans for the large 500-mm. triangle on which to plot such diagrams. That would not do as a base, because it is badly distorted. We therefore started from scratch with an entirely new plate, engraved on copper. We then made the drawings on a metallic base so that there would be no distortion and registration would be perfect, and then turned the drawings over to the mapmaking company to make the reproductions.

We have made a beginning with the four ternary systems of the oxides: silica, alumina, lime, and magnesia. On the sides of the ternaries will be found the temperature and composition data for the six binary systems at the same time. The reproduction is in black and three colors; black showing the fields of the primary phases; red, the compounds and solid solutions and the triangles which define the ultimate crystalline phases; green, the contours that show the temperatures of complete fusion; and blue, the basic triangle of percentage composition by weight.

I need not go into detail as to what is on the diagrams, because they are familiar to most of you. This reproduction now makes them available on a large enough scale so that we can interpolate to one-tenth of one per cent with some confidence. If you like maps, you will be interested in these simply as a mapmaking job; the printing of four colors in this size and making them register within a fraction of a millimeter, which is necessary if we would interpolate a tenth of a per cent, takes skillful work, and the mapmakers have done a very nice job.

The cost of such work is too large to justify its being underwritten by one organization alone, but we assumed that other laboratories would be interested to share the cost with us, and we have therefore run off some extra copies, available for sale at \$2.00 for the set of four, expecting that this will cover about one-half the cost of reproducing the diagrams. The blue triangle will also be available, if anybody would like to get copies of it.

F. B. FOLEY.—Why was high-frequency induction furnace melting neglected? Because there is no slag on it?

G. B. WATERHOUSE.—That is a very good question. Several men have already asked who would discuss that particular phase of the subject, the question of the slag control in high-frequency electric-furnace melting. If any here wish to contribute to that, I know it would be very much appreciated, whatever they care to say.

B. STOUTON,* Bethlehem, Pa.—Has there been in this country any special slag control in high-frequency furnaces? In Europe a good deal has been done in that line, and some wonderful results have been obtained in refining pig iron, turning out 24 heats in 36 hr., and getting rapid circulation of the bath. But so far as I know there has been no real slag control in this country. .

F. B. FOLEY.—It has been our observation in induction-furnace melting that the charges that carry elements of a chromium type, high-chromium content, tend to protect the iron from oxidation, and that, generally, cleaner steels of the high-alloy type are produced than of the pearlitic type. The pearlitic types of steel have few

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elements present to protect the iron from oxidation, and, because of the churning effect of the process of melting, almost all of the metal comes in contact with the air. A great amount of oxidation occurs in this way. The difficulty with slag, of course, is obvious. The top of the metal is exposed to the air, and anything put on the bath in the way of a slag chills. There is a very low temperature at the surface of the slag, and only the slag-metal interface attains a high temperature.

The type of crucible used has a considerable bearing on the slag problem in the induction furnace. The metal, being in continuous motion, erodes the crucible and probably picks up nonmetallic impurities. Has any one here had any experience with slags that would pick up nonmetallic particles and remove them from the metal as it passed by? There appears to be little to be gained in cleanliness of the metal by allowing the metal to lie still with the hope that nonmetallic matter will float out.

A. B. KINZEL.—It should be mentioned that the stirring action in some induction furnaces is so vigorous that the probability of entrapping slag would appear to be as great as that of eliminating slag from the metal.

B. STOUGHTON.—So much has been said about oxidizing slags in electric furnaces, I should like to know whether it is the opinion of the electric-furnace makers at the present time that they can make really high-quality steel after using an oxidizing slag. It has always been said that if there is an oxidizing slag, no matter how carefully the bath may be reduced afterwards, the steel is not of top-notch quality. I wonder whether steelmakers have changed their opinion on that point.

A. D. PORTS.—It has been my experience that steel must be oxidized to the point where the bath is stirred by a good boil due to the evolution of CO. Then you can go ahead and start to reduce.

B. STOUGHTON.—You do not have to oxidize it if you use raw materials that do not require silicon or phosphorus or other elements removed. That is certainly the practice in a great many of the best plants.

H. F. WALTHER.—I do not think that there is sufficient scrap available low enough in silicon and phosphorus to put electric steelmaking on a commercial or competitive basis, by melting without some necessary oxidation. A normal melt in a furnace is always slightly oxidizing. The scrap can be melted without oxidation, but entails the use of silicon in the charge, and from our experience the resultant product has been very unsatisfactory by this latter practice. I do not presume to say that we tap our steel on the melt-down slag. It is removed. The metal is finished under an extremely deoxidizing type of carbide slag.

Manufacture and Properties of Bessemer Steel

By C. C. HENNING,* MEMBER A.I.M.E.

(New York Meeting, February, 1935)

In any line of human activity logical handling requires an amount of attention to each phase that is in keeping with the importance of that phase. In the complex and rapidly changing field of modern ferrous metallurgy it is difficult to allot the proper degree of attention to the various subjects, and it is not surprising that one or more subjects of major importance should for a time be neglected.

Bessemer steel is a good example of a neglected subject. It is largely taken for granted, inferior physical quality is assumed for it, and there is a lack of interest in its technical development and commercial application. Availability of supply is limited. In spite of this technical indifference, limited source and lack of commercial exploitation, bessemer steel constitutes a large volume of tonnage in daily use. There is a fairly prevalent idea even among technical people that bessemer steel survives mostly because of low cost and by reason of a dwindling residue of applications sufficiently common to permit of its use.

The difference in cost between bessemer and open-hearth steel is governed largely by the relative cost of manufacture of pig iron and the market price of steel scrap. During the past four years there have been long periods of time during which the price of steel scrap was low enough so that open-hearth steel was considerably lower in manufacturing cost than bessemer. As to application, it may be pointed out that thousands of tons of this material in the form of bessemer screw steel are applied for moving parts in automotive and other equipment. Some forging work and considerable heat-treating, particularly carburizing, is performed on this grade.

From an economic standpoint the most effective contribution of bessemer steel lies in its free machining qualities. It is by far the freest

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machining steel available and it is no exaggeration to state that this property alone has been a tremendous economic factor in the cost, production, and use of a great variety of manufactured articles requiring a large amount of machine work, which otherwise could hardly have been produced in the volume and price at which they have been distributed. Although this is probably the outstanding quality of bessemer steel that enables the bessemer converter to retain its place in the steelmaking sun, the steel has other highly desirable qualities of demonstrated superiority to open hearth that make it a valuable contribution to engineering materials. Some of the qualities particularly worthy of mention are weldability and stiffness; also its pronounced reaction to cold work in certain applications.

While it is generally understood, it should be emphasized that a significant difference exists between European and American bessemer practices. The American practice is acid, in which a siliceous lining is used in the converter and no attempt is made to work phosphorus and sulfur. The European practice, on the other hand, is to use a basic lining and basic slag, with an after-blow which accomplishes some reduction in phosphorus and sulfur. This practice is necessary with high-phosphorus ores and is sustained to some large degree by high-phosphate slags, which are an appreciable and valuable byproduct of the process. The phosphorus content of the finished steel is appreciably lower than in the American acid process, but the quality of the product is not greatly different from the American acid bessemer steel.

This paper proposes to review briefly the making of steel by the acid bessemer process, the progress of its manufacture, developments of existent practices, and to discuss certain of the outstanding quality factors of bessemer steel, as well as the future possibilities of the bessemer process, with the idea of extending interest in this very important branch of steelmaking.

PRESENT STATUS OF BESSEMER PRODUCTION

Little has been said or written about the bessemer process during the past 10 years, yet during these latter years there has been convincing evidence that the bessemer plant is a very important unit of the steel industry. This condition, as well as the present status as gaged by relative tonnage production during the past 9 years, is best indicated by the tonnages in Table 1.

Any process that consistently produces over a million tons of ingots per year must be recognized as important. As indicated, the combined acid open-hearth, electric-furnace and crucible tonnage is considerably less than one-fourth of the bessemer tonnage produced, yet more is heard about the acid open-hearth and particularly the electric-furnace process than about the bessemer.

TABLE 1.—*Tonnage of Steel Ingots by Different Processes*

| Year | Open Hearth | | Bessemer | Electric Furnace | Crucible | Total |
|------|-------------|---------|-----------|------------------|----------|------------|
| | Basic | Acid | | | | |
| 1925 | 36,632,060 | 484,843 | 6,670,128 | 335,978 | 17,729 | 44,140,738 |
| 1926 | 30,172,688 | 533,285 | 6,891,502 | 325,278 | 13,452 | 46,936,205 |
| 1927 | 36,750,387 | 493,653 | 6,153,703 | 371,278 | 7,696 | 43,776,717 |
| 1928 | 42,818,557 | 454,883 | 6,591,745 | 453,692 | 6,516 | 50,325,393 |
| 1929 | 46,644,206 | 576,393 | 7,091,680 | 532,392 | 5,762 | 54,850,433 |
| 1930 | 33,898,518 | 367,181 | 5,020,588 | 307,418 | 1,563 | 39,595,268 |
| 1931 | 21,986,933 | 194,388 | 3,011,394 | 235,376 | 831 | 25,428,922 |
| 1932 | 11,689,495 | 104,794 | 1,528,544 | 141,328 | 241 | 13,464,402 |
| 1933 | 19,972,805 | 195,495 | 2,425,779 | 299,808 | 399 | 22,894,286 |

Considerably more bessemer-blown metal is used annually in connection with the open-hearth practice (duplex metal) than is produced in either the acid open-hearth or electric furnace in the form of ingots. In fact, in 1930 the bessemer steel used for this purpose amounted to 2,045,277 tons, which was more than three times greater than the combined tonnage made in the electric-furnace and acid open-hearth practices. These facts further indicate that aside from its direct production the bessemer is an important unit to the industry as an auxiliary to open-hearth operations.

Another interesting feature is the comparison in Table 2 of bessemer ingot tonnage with the total tonnage (all processes) of alloy steel. The relationship shown might be a little surprising at first glance

TABLE 2.—*Tonnage of Bessemer-steel Ingots vs. Tonnage of Alloy-steel Ingots*

| Year | Bessemer Ingots | Alloy-steel Ingots | Year | Bessemer Ingots | Alloy-steel Ingots |
|------|-----------------|--------------------|------|-----------------|--------------------|
| 1925 | 6,670,128 | 2,320,390 | 1930 | 5,020,588 | 2,317,183 |
| 1926 | 6,891,502 | 2,317,313 | 1931 | 3,011,394 | 1,366,010 |
| 1927 | 6,153,703 | 2,385,904 | 1932 | 1,528,544 | 757,560 |
| 1928 | 6,591,745 | 3,045,225 | 1933 | 2,425,729 | 1,475,400 |
| 1929 | 7,091,680 | 3,764,287 | | | |

because so much has been written about alloy steels and so little about bessemer steels. It would be interesting to know just what the comparative tonnage ratings of these processes and steels would be now if the same amount of thought, research and development effort in proportion to its tonnage importance had been applied to the bessemer plant. The results of such research and development might well pay surprisingly large dividends.

BESSEMER PRODUCTS

A very large percentage of the bessemer steel manufactured today goes into screw steel, sheet steel, tin plate, wire, skelp for welded pipe, and bars for bolts, nuts, concrete reinforcing, track spikes and small structural and special shapes. Some typical chemical specifications for these various applications are given in Table 3. This list is only partial,

TABLE 3.—*Bessemer Chemical Specifications*

| Product | Percentages Required | | | |
|--|----------------------|--------------|--------------|----------------|
| | Carbon | Manganese | Phosphorus | Sulfur |
| Screw steel (standard grade). | 0.08 to 0.16 | 0.60 to 0.90 | 0.09 to 0.13 | 0.100 to 0.180 |
| Screw steel (high-sulfur grade)..... | 0.08 to 0.16 | 0.60 to 0.90 | 0.09 to 0.13 | 0.200 to 0.300 |
| Screw steel (high-carbon grade)..... | 0.25 to 0.35 | 0.60 to 0.90 | 0.09 to 0.13 | 0.100 to 0.180 |
| Skelp..... | 0.08 max. | 0.30 to 0.60 | 0.11 max. | 0.08 max. |
| Bars, track spikes, sheet and tin plate..... | 0.10 max. | 0.30 to 0.50 | 0.11 max. | 0.07 max. |
| Soft wire..... | 0.12 max. | 0.60 max. | 0.11 max. | 0.08 max. |
| Medium wire..... | 0.10 to 0.20 | 0.70 max. | 0.11 max. | 0.08 max. |
| Reinforcing bars..... | 0.15 to 0.35 | 0.70 max. | 0.11 max. | 0.08 max. |
| Structural soft..... | 0.07 to 0.12 | 0.30 to 0.60 | 0.11 max. | 0.08 max. |
| Structural medium..... | 0.25 to 0.35 | 0.30 to 0.60 | 0.11 max. | 0.08 max. |
| Structural high-tensile..... | 0.35 to 0.45 | 0.30 to 0.60 | 0.11 max. | 0.08 max. |

as there are many modified chemical specifications designed for specific purposes, but it will serve to indicate the broad field as well as to reveal some of the many high-quality applications being made regularly of bessemer steel.

Bessemer steel has been frequently condemned entirely on theoretical grounds, and in many cases unjustifiably so. In many applications bessemer steel is never considered, although it may fit the requirements better than steel made by other processes. This situation is a result of lack of development and lack of dissemination of data by the manufacturers, who too frequently overlook or neglect the creditable features of bessemer steel. It is quite possible that if more technical data were available on bessemer steel, it would assist in arriving at a more accurately suitable selection of quality, and in many cases a bessemer grade might be found desirable or superior for a specific type of service performance.

BESSEMER IRON

The factors needful for the production of pig iron best suited for bessemer blowing arise from variables that affect the uniformity of blast-

furnace conditions and include the close and detailed control of burden, temperature, physical and chemical conditions of the coke, humidity, slag volume and analysis, and other conditions, which vary from day to day or cast to cast. Smooth furnace operation is highly important, not only from the standpoint of maintenance of uniform iron analysis and temperature, but also from the standpoint of minimizing the amount of unreduced oxides in the iron. Erratic progress of analysis from cast to cast, even though within the specification range and although modified analytically by mixing with other casts to produce an ideal analysis, will usually give poor results in the finished steel.

Iron either physically hot or with a high silicon content will induce high temperature during blowing and may result in poor surface and excessive tendency toward piping. The opposite of this condition is represented by physically cold iron with low silicon content, and this is apt to be sluggish and dirty, producing dirty steel with tendencies toward scabbiness and generally poor rolling quality. Intermediate between these extremes is an optimum condition of uniformity of iron analysis with physical temperature within a reasonable range and balanced fairly well with silicon content to produce a uniform steel temperature.

IRON ANALYSIS AND TEMPERATURE

While there is a variety of opinion on the most suitable iron analysis for bessemer blowing, due to differences in set-up for handling and local conditions, the following chemical limits closely represent present-day specifications: carbon, 4.0 to 4.5 per cent; manganese, 0.70 max., phosphorus, 0.08 to 0.10; sulfur, 0.05 max.; silicon, 1.00 to 1.75. This analysis, particularly with respect to manganese and silicon, will vary somewhat with the grade of steel being made. In blowing bessemer screw steel it is good practice to hold the manganese to 0.50 per cent maximum, preferably under 0.45 per cent. The phosphorus should not run much over 0.09 per cent and sulfur should be as low as possible, because these elements are not oxidized in the acid bessemer process and an increase of about 10 per cent over the iron analysis may be expected in the steel.

Manganese Content of the Iron.—Iron with normal silicon (1.10 to 1.50 per cent) but with manganese of 0.45 to 0.50 per cent results in fairly liquid slag, and with increasing manganese above this range there is considerable loss of metal due to slopping; also the ladle reaction is inefficient, resulting in poor quality in the finished steel. While there has been discussion about the proper manganese content of bessemer iron for the manufacture of bessemer screw steel, yet there are very few data available as to the actual effect of manganese in bessemer iron on the quality of steel produced. In order to develop this feature a comprehensive study involving nearly 100,000 tons of billets was made, with the results shown in Table 4.

This study indicates that there is a definite penalty attached to using iron with manganese over 0.45 per cent and also a resultant poorer quality steel. Iron with manganese content of about 0.50 per cent is apparently the critical point in blowing quality of bessemer iron; the point at which watery slags and slopping are encountered. Better ladle reactions, better slags, and more uniform results are obtained with low-manganese bessemer iron.

TABLE 4.—*Effect of Increased Manganese in the Iron*

| Manganese Content, Per Cent | Results of Billet Chipping | |
|-----------------------------|----------------------------|------------------|
| | Rejections | Tons per Man Day |
| Under 0.45..... | Normal | Normal |
| 0.45 to 0.50..... | 2.1 increase | 0.4 decrease |
| 0.50 to 0.55..... | 8.8 increase | 1.2 decrease |
| 0.55 to 0.60..... | 10.0 increase | 1.9 decrease |

Sulfur Content of the Iron (Residual Sulfur).—High-sulfur iron, producing high residual sulfur in bessemer steel, is conducive to poor rolling quality to the same extent as with high residual sulfur in open-hearth steel. The effect of high residual sulfur is red shortness in rolling, resulting in increased cracks and seams in the billet surface. Poor rolling quality from this source is also displayed in the manufacture of high-sulfur grades. A study of over 150 high-sulfur blows revealed that the lower the residual sulfur the better the rolling quality of the steel. In addition, experience indicates that there are reasons for believing that excessively high residual sulfur may adversely affect machinability. Efforts are made to keep the residual sulfur in bessemer steel as low as practicable and it is considered good practice to hold this element between 0.030 to 0.040 per cent in the iron. With sulfur much under 0.030 per cent other variables are introduced which affect bessemer blowing.

Iron Temperature.—It has been found generally advantageous to charge iron at a temperature of 2200° to 2350° F., and the more uniform this temperature is maintained from charge to charge, the smoother will be the bessemer operations.

IMPORTANCE OF MIXER

Molten iron may be sent direct from the blast furnace or from a cupola and charged in the bessemer converter, but the usual and more advantageous practice is to utilize to the fullest extent the desirable operating and quality benefits of the mixer. The hot-metal mixer is in reality a storage reservoir for molten iron and is indispensable to the making of bessemer steel in times of intermittent operations such as

the steel industry has experienced during the past four years. The benefits derived from the mixer are: (1) conservation of heat in the pig iron, keeping the metal molten; (2) delivery to the converter of iron more uniform both chemically and physically, than in separate furnace casts; (3) minimized offcasts: casts slightly high or low in analysis or temperature for best blowing may be mixed with other iron of correct analysis and temperature, making available a larger tonnage suitable in analysis and temperature; (4) some reduction in sulfur is accomplished under certain conditions. The iron in the mixer is usually held at a temperature of 2200° to 2400° F.

CONVERTERS

The size of converters in this country ranges from 10 to 25 tons. The older units, for the most part, are of about 10 tons capacity, and the latest converters built are about 25 tons. From a quality standpoint, experience with both sizes has not indicated any appreciable difference within this size range, and there are production advantages for the larger units. Converter plants in Europe range up to 45 tons and there is little if any reason to feel that this is beyond the optimum size from a quality standpoint. At one plant in this country it is the practice to pour the contents of two 25-ton converters into one ladle, thus making 50-ton bessemer melts.

As to construction, except for a number of side-blow converters attached to steel foundries, bessemer converters are bottom-blown with bodies slightly curved and with the mouth either eccentric or concentric with the bottom. The traditional cylindrical stack to carry the flame above the building has largely disappeared. One recent installation consists of two 25-ton converters of the bottom-blown, curved body, tilting, eccentric type, and in this plant provision is made for an extra or spare converter so that relining of the shell involves only the simple operation of installing the spare converter with almost uninterrupted operations. The average life of a converter lining is about 800 heats.

Under good practice from 25 to 35 heats should be made on a single bottom and it should require less than one hour to change a bottom. There is a tendency to erode at the tuyeres, and it becomes necessary during the life of a bessemer bottom to blank off or close some of these openings. This tends toward nonuniformity of blowing action throughout the vessel and if too many blanks are inserted it prolongs the blowing period. In some plants there is a standing rule that no more than five blanked tuyeres shall be used in a bessemer bottom, but in others the number of blanks may run up to eighteen before bottom is changed.

THE BESSEMER PROCESS

There are no extraneous fuels in the bessemer process and it is the only steelmaking method in which the charge must be liquid. The charge

must also be within fairly narrow chemical limits. The total blowing time for 10 to 25-ton converters is from 10 to 20 minutes.

The refining process of the converter is best portrayed by Table 5, which is fairly representative of iron with normal analysis.

TABLE 5.—*Removal of Metalloids*

| Element | Initial Charge, Per Cent | Time of Blowing | | | | |
|-----------------|--------------------------|-----------------|-------|-------|-------|-------|
| | | 2'0" | 3'30" | 6'0" | 8'10" | 10'0" |
| Carbon..... | 4.30 | 3.90 | 3.75 | 2.10 | 0.60 | 0.03 |
| Silicon..... | 1.25 | 0.70 | 0 38 | 0 03 | 0.03 | 0.005 |
| Manganese..... | 0.40 | 0.10 | 0 04 | 0 03 | 0.01 | 0.01 |
| Phosphorus..... | 0.085 | 0 088 | 0 090 | 0 092 | 0 094 | 0.096 |
| Sulfur..... | 0.035 | 0.035 | 0 036 | 0.037 | 0.038 | 0.039 |

Silicon is the first element to be oxidized, next the manganese. Coincidentally some iron is also oxidized, forming a slag containing iron oxide and manganese oxide. So long as silicon and manganese are present, very little carbon burns. Phosphorus and sulfur in the metal are not removed because the acid slag will not dissolve them even if they become oxidized, and these two elements are increased slightly as a result of weight loss in blowing.

Analysis of Bessemer Slag.—A typical slag analysis (bessemer screw steel) taken from a converter at the end of a blow, together with the analysis of the ladle slag from the same blow, is given in Table 6.

TABLE 6.—*Bessemer Slag Analyses*

| | Slag Analyses, Per Cent | |
|----------------------|-------------------------|------------|
| | Converter Slag | Ladle Slag |
| Silica..... | 67.60 | 50.30 |
| Alumina..... | 2.12 | 1.33 |
| Ferrous oxide..... | 16.32 | 18.77 |
| Ferric oxide..... | 2.91 | 2.99 |
| Manganese oxide..... | 10.00 | 24.09 |
| Lime..... | 1.05 | 2.45 |
| Magnesia..... | Trace | Trace |

The lime and magnesia are a result of a small amount of blast-furnace slag which usually finds its way into the converter.

Bessemer Yields.—A converter yield of 91 to 92 per cent is considered good practice. This loss of 8 to 9 per cent represents the difference between the charged weight and the steel ingots and is divided about as

shown in Table 7. These figures will vary somewhat, depending upon the analysis of the charge and the end point in blowing.

TABLE 7.—*Losses in Bessemer Steelmaking,*

| | PER CENT |
|------------------------------|------------|
| Carbon burned..... | 4 30 |
| Silicon burned..... | 1.25 |
| Manganese burned..... | 0.40 |
| Fe in slag and pellets..... | 1 50 |
| Ejected and volatilized..... | 1.00 |
| | <hr/> 8.45 |

Cooling the Blow.—Our experience indicates that iron with silicon much under 0.95 per cent results in a cold blow and usually requires side blowing, a practice that should be avoided for best quality of steel surface. Iron chemically hot, that is with silicon over 1.60 per cent, will result in temperature in excess of the desirable teeming range. There are two recognized methods of cooling the blow; namely, adding scrap to the vessel or blowing steam through the metal. An investigation favored the former practice to the extent of 10 per cent lower chipping rejections. From a quality standpoint, adding scrap is preferable, and additions can range up to 15 per cent of the charge. The conversion of scrap into steel by adding to the vessel constitutes an economic advantage also in times of low scrap cost. In general, steam is used in all bessemer shops to some degree for the purpose of cooling the metal, but the disadvantage of excessive steam from a rolling standpoint is fairly well recognized and an effort is made to hold steaming to a minimum. The practice of scrap cooling so as to finish with a little ladle skull which corresponds to a teeming temperature of about 2800° to 2900° F. is desirable.

Blowing.—From an operating standpoint the crux of the operation is in the point at which oxidation or blowing is stopped. Every bessemer plant and operator has slightly different opinions on the end point for blowing. In some plants the aim is to blow "young"; that is, to cease blowing very early after the removal of metalloids, to minimize oxidation. In other plants the practice is to blow "full," so as to induce greater action from the ladle additions. Just which is to be followed depends upon the grade to be made and the final quality of the steel. With a bessemer plant operating steadily, and considering that blows are produced in rapid succession, it should not take long to determine the best practice to be used on a specific grade.

Holding Ladle.—In bessemer steelmaking there is pronounced interaction between metal and slag, not only on account of the chemical reactions involved but because of the mechanical mixing generated by the air currents flowing through the molten mass and the lack of separation of metal and slag when these are being poured into the ladle. For

this reason there will normally be a greater admixture of slag in the steel. The period from ladling to pouring into the ingot molds gives some opportunity for the slag to clear out of the steel, and in some cases this interval is purposely extended to permit greater cleaning effect and temperature drop.

Recarburization.—The bessemer tonnage produced today is largely in low-carbon grades (carbon under 0.20 per cent), therefore very little recarburization is done in the bessemer process except that which is accomplished through ferromanganese additions. With respect to the ferromanganese additions, the practice varies somewhat, especially where the minimum manganese specification to be met is above 0.50 per cent. In some plants a furnace is provided for heating manganese to about 1000° to 1500° F. In other shops the practice is to wet down the manganese so that the steam generated when contact is made with the molten slag will blow the slag away, thus minimizing the possibility of entrapping manganese in the slag. In some cases also the manganese is screened to a maximum size of about 1½-in. The latter is considered good practice.

In high-carbon specifications, catching carbon coming down is so difficult that it is not ordinary practice. For grades requiring carbons higher than 0.15 per cent molten iron seems to give the best results and is preferred to other means of recarburizing, such as the use of crushed anthracite coal or coke dust. Molten iron in general is more dependable than other recarburizers.

Additions.—Additions are made at various points. Scrap additions for cooling are added to the converter, as are pyrites additions in making screw steel and also copper additions for making copper-bearing steels. Recarburizers such as ferromanganese or other additions to make specifications are added to the ladle. Mold deoxidation or semi-killing is also practiced, using usually shot aluminum or fine 50 per cent ferrosilicon.

Sulfur Additions.—To develop the merit of various means of making sulfur additions to bessemer screw steel (sulfur, 0.100 to 0.180 per cent) a long-time experiment involving over 50,000 tons of this grade was inaugurated. A direct comparison of steel made with iron pyrites as a converter addition and flowers of sulfur as a ladle addition, by billet chipping, showed that with flowers of sulfur rejections and tons per man day were both normal while with iron pyrites rejections showed 3.5 per cent decrease and tons per man day, 1.2 increase. As indicated, a yield saving of 3.5 per cent, as well as a faster chipping rate, was realized from the iron pyrites practice.

In addition to the improved surface, the final product was considerably improved generally. Chemical determinations showed a noticeable uniformity of sulfur content throughout the ingot and blow, which was revealed by check analyses made on billets representing the top, middle

and bottom of the first, middle and last ingots poured on a representative number of blows. Deep etch tests and microscopic examination have in general indicated a more uniform distribution of sulfide inclusions than found in steel made with flowers of sulfur, and routine machinability tests have shown consistently more satisfactory and uniform results. In this case it may reasonably be questioned whether the benefits derived were due to the combined form of the addition or to the fact that its addition to the converter permitted of greater diffusion throughout the metal. In any event the use of iron pyrites as a sulfur addition in the manufacture of bessemer screw steels has resulted in a distinct quality improvement.

Capped Steel.—Bessemer plants in many instances have clung fairly closely to the bottle-top mold with a cap fitting neatly in the bottle neck of the mold. This cap may be secured with a key. In this pouring practice the steel is not killed and the cap, through chilling action on the top of the ingot, prevents full rimming action or growth. In a quality sense, capped steel probably lies between killed and rimmed steel, approaching more closely the quality of the rimmed. A variation from mechanical capping, which provides for about equivalent quality, is to kill with 50 per cent ferrosilicon about 40 mesh, usually in the extreme top portion of the ingot. This has the effect of killing the action of the steel in the upper part of the mold, which freezes promptly so as to inhibit open rimming action. Silicon is always used as a deoxidizer in bessemer screw steel in preference to aluminum and usually it is sparingly added. The addition of one pound or less per ton is considered good practice. Blows with low carbon and manganese contents, and consequently greater amounts of iron oxide in solution, will require larger amounts. The use of ferrosilicon instead of aluminum on pouring platforms of bessemer plants is in contradistinction to the practice on open-hearth pouring platforms where aluminum is used almost solely for mold deoxidation. It may be said in its favor that the products of ferrosilicon mold deoxidation are less detrimental for machining, surface, and other reasons than the products of aluminum. Aluminum, however, is usually used for deoxidizing low-sulfur grades.

Rimmed Steel.—Bessemer steel cannot be classified as an ideal rimming steel in comparison with the same carbons on open-hearth steel, but where bessemer shop and track space permit, a fairly high percentage of the lower carbon grade is rimmed. Our experience indicates that low-carbon bessemer grades can be rimmed as well as equivalent open-hearth steels; that is, open-hearth steel with carbon 0.12 to 0.20 per cent. Temperature and oxidation conditions are usually at an optimum for rimming action and on suitable grades a definite appreciation in surface and ductility over killed steels can be expected from this practice. In addition, it will usually be found that a greater uniformity will be attained in both of these qualities.

The mechanical jarring of ingots is a development designed to accentuate rimming action, and by this method it is now practicable to rim grades that heretofore were killed. With the aid of this equipment it has been our experience that a deeper and more uniform rim is obtained in the ingots, as well as more consistent production and quality results from heat to heat. Rimming ingots by jarring in grades that are ordinarily semikilled resulted in an increased billet yield of 1.6 per cent, a reduction in chipping rejections of about one-fourth, and an increase of 3.0 tons per man day in the chipping rate. Surface requirements of the steel involved in this comparison were fairly exacting and difficult of uniform attainment, and the results in general revealed a greater uniformity of surface throughout the melt.

Killed Steel.—On this variety of bessemer steel probably more variability of rolling results is encountered than on either the rimmed, semikilled or capped grades. Where the steel must be fully killed, losses because of poor surface are apt to be excessive at times. In such cases, and when reladling is possible, some advantage may be found in adding the large percentage of deoxidizers to the ladles and holding them as long as the temperature of the metal will permit, to allow for optimum fluxing of deoxidation products through the metal to the slag.

Teeming (Nozzle Size).—Nozzle sizes used for pouring range from $1\frac{1}{2}$ to $2\frac{1}{2}$ in. There is a strong tendency to prefer the smaller nozzle sizes for quality reasons, and from the standpoint of temperature it is reasonable to believe that no difficulty would be found with skulls from this practice on bessemer steel. As to temperature in general, it is a truism among operating men that a clean bessemer shop is a sign of poor bessemer steel, which refers to the fact that if skulls are not found in occasional blows, it is a sign that pouring temperatures are in excess of the range for best quality bessemer steel. This matter of nozzle size was investigated on some two hundred blows. It was revealed that after pouring a number of blows, equivalent to about 80 tons, the nozzle increased through erosion approximately 50 to 60 per cent and that the chipping rejections were less on the first 40 tons poured as compared to the last 40. Nozzle sizes ranging from $1\frac{3}{4}$ to $2\frac{1}{8}$ in. seem to be a good "all-purpose" practice for general use on the majority of bessemer grades.

Mold and Mold Temperature.—The set-up as to mold size and design for the bessemer plant is very similar to that for the open-hearth shops. Molds as a rule may be used interchangeably on bessemer and open-hearth steel and in general there are no major differences in the size or design of mold for either steelmaking process. The only exception is that bessemer plants probably retain to a greater degree the bottle-top type of mold referred to previously.

The same precautions for proper mold temperature used in the open hearth apply to bessemer steelmaking in every detail. The opinion as

to best mold temperature varies somewhat, but a temperature of 200° to 400° F. is good practice. Under normal operating conditions an average mold rotation of 11 hr. results in satisfactory mold temperature; that is, to use the molds every 11 hr. Mold temperature obtained in this manner, because it insures greater uniformity of mold temperature, is much preferred to artificial heating.

Duplex Metal.—Under normal operations considerable tonnage of bessemer metal or semifinished product is blown and delivered in molten form to the open hearth for further refinement into open-hearth steel. This product is usually blown from low-manganese basic iron of about the following specification: C, 4.0 to 4.5 per cent; Mn, 0.70 max.; P, 0.40 max.; S, 0.05 max.; Si, 1.00 to 1.75.

In blowing basic iron the same order of oxidation and elimination of the elements takes place as in blowing bessemer iron; that is, the silicon first, then the manganese and carbon. Phosphorus and sulfur are increased slightly. "Blown metal," as this product is referred to, is ordered from the bessemer department by the melter in the open hearth as high carbon or low carbon. The high-carbon order is filled by blowing very young and represents metal with carbons about 0.40 to 0.80 per cent while the low-carbon is full blown with carbons about 0.02 to 0.04 per cent. Essentially the duplex operation consists of the use of molten bessemer metal of controlled carbon content, instead of the miscellaneous cold scrap of variable analysis and origin ordinarily used in open-hearth operations. Open-hearth steel manufactured by the duplex process is a very interesting subject, from both a steelmaking and quality standpoint, but is not considered a part of this paper.

Aston Process.—The Aston process for manufacturing wrought iron has as its base bessemer-blown metal, which in the molten state is poured slowly into a thimble of slag. The resultant mass with excess slag squeezed out is rolled into skelp and bar products. Physical qualities and corrosion resistance comparable with hand-puddled wrought iron are claimed for this product. It is perhaps as apt an illustration as one might find of the quality control that is capable of achievement in the bessemer process, and is all the more remarkable when one takes into account that it is achieved through the addition rather than the elimination of slag particles.

FLEXIBILITY OF BESSEMER PROCESS

Aside from the useful quality characteristics of the metal, which will be discussed presently, the bessemer process from the steelmaker's viewpoint has certain operating advantages over open-hearth. It has been shown earlier in this paper that delays for replacement of bottoms or of the vessels themselves are of minor length as compared with the weeks during which open-hearth furnaces must be rebuilt. However,

the outstanding advantage rests in the flexibility of making small tonnages in different grades of steel. In a single converter it is possible to make three grades of steel in less than one hour. This feature has been particularly desirable during the past four years because of the pressure of quick delivery of orders for small tonnage.

PRESENT STATUS OF BESSEMER QUALITY

From a quality standpoint the bessemer excels in certain useful characteristics such machinability, stiffness, weldability, and an intense reaction to cold work. These properties are inherent to the process, and while they have not been thoroughly understood until recent years, it is safe to say that at least some of these characteristics are controllable within certain ranges and for specific applications. Table 8 gives a rough comparison of some of these inherent bessemer characteristics with equivalent open-hearth steel.

TABLE 8.—*Quality Comparison*

| | Machinability, Per Cent | Stiffness, Per Cent | Weldability, Per Cent | Sensitivity, Per Cent |
|----------------------|-----------------------------------|------------------------|--|--|
| Bessemer..... | 100 | 100 | 100 | 100 |
| Open-hearth..... | 75 | 85 | 90 | 80 |
| Basis of rating..... | Commercial machining tests. | Deflection tests | Hot-welding, mainly lap and butt-weld pipe. | Marked change in physical properties by cold-working. |

Certainly from a quality standpoint the bessemer still holds a considerable margin in a number of very important factors. Machinability particularly has been given considerable attention during the past several years, with marked improvement. The marked sensitivity of bessemer steel to cold-work enables bessemer screw steel to hold its leading place in the race for free-cutting efficiency. This property and the aging characteristics of bessemer, as well as the other useful quality features, are receiving belated study; for each of them is capable of useful applications.

REASONS FOR SUPERIOR QUALITY

There are several theories to explain some of the inherent quality differences between open-hearth and bessemer steel. The most obvious reason is, of course, the difference in phosphorus content, as shown by the ordinary analysis. However, open-hearth steels rephosphorized to the same analysis as bessemer do not possess bessemer characteristics. In the oxidation of the bessemer process lies another fairly plausible source of these quality differences. We believe that nitrogen is the most significant element, although its effect may be accentuated to some degree by the

higher phosphorus and greater oxidation. Nitrogen contents of bessemer steel, which are definitely and substantially higher than open-hearth, bear some evidence in this direction. Elaborating on the extent of these quality differences we are submitting some comparisons which indicate average or typical differences with open-hearth steel.

Machinability

There is no grade yet developed that even closely approaches the potential high-speed cutting qualities of the bessemer screw steels, and for this reason it is today one of the major tonnage outlets for the bessemer. Roughly, the machinability of bessemer screw grades compared with grades commonly used in machining operations may be conservatively listed as shown in Table 9. This comparison is given only as a rough index of the comparative machinability of the grades shown when machined at light feeds and fast speeds, which is a practice commonly used on bessemer screw steel. With increased feeds, and particularly with relatively heavy feeds, these ratings will change considerably.

TABLE 9.—*Machinability Comparison*

| GRADE | RATING, PER CENT |
|---|------------------|
| Bessemer screw (high-sulfur)..... | 120 |
| Bessemer screw (S.A.E. 1112)..... | 100 |
| Open-hearth manganese screw (S.A.E. X 1315)..... | 85 |
| Open-hearth screw (S.A.E. 1120)..... | 70 |
| 0.15 to 0.25 carbon open-hearth low-sulfur (S.A.E. 1020)..... | 50 |
| 0.10 to 0.20 carbon open-hearth low-sulfur (S.A.E. 1015)..... | 40 |

During the past several years a considerable amount of investigational effort has been applied to the manufacture of bessemer screw steel, and the result has been a greatly improved and superior product. This improvement has not been accomplished solely by the adjustment in analysis, but mainly by refinements in the control of the steelmaking methods, which has resulted in practices better designed to minimize the amount of inclusions that have been found to be detrimental to machinability. As a result of these advancements, the average machinability of bessemer screw-steel grades has been increased upward of 15 per cent and the uniformity of machining qualities from blow to blow has been greatly improved.

In the matter of machinability the manufacturer is striving constantly to accomplish two improvements: (1) to increase the average machinability of his product and (2) to minimize the scatter or variation in machinability from blow to blow. Desirable progress already has been made in both these problems, particularly the former, and the possibilities for further improvement are highly favorable. In fact, today bessemer screw may be considered one of the most important products of the steel industry in which positive metallurgical advancement has been made,

and on which the improvements are being commercially and successfully applied to the benefit of the consuming trade. Further improvements will be accomplished and it is likely that the machinability of bessemer screw steel will be increased far beyond its present limitations.

Stiffness

Bessemer steel, because of its high phosphorus content, gives considerably higher tensile strength than equivalent carbons in open-hearth steel. The spread in carbon for similar tensile strength amounts to about 10 points; that is, normally a 0.10 per cent carbon bessemer steel will give tensile strength of about 60,000 lb. per sq. in., whereas to obtain this same tensile in open hearth it requires steel of about 0.20 per cent carbon. This carbon spread will vary slightly in the various grades but with other elements normal the 10-point difference is usually considered a good working basis. It is well known, however, that bessemer steel, both hot-rolled and cold-drawn, in general is stiffer than open-hearth steel of equivalent tensile properties. This difference in stiffness when judged by the yield point, which usually is slightly higher on bessemer steel, does not indicate the real significance of this inherent bessemer quality.

A statement that soft bessemer steel and bessemer screw steel are stiffer than 0.40 to 0.50 carbon open-hearth grades, when tested for resistance to deflection or under certain service performance, may seem difficult to appreciate, yet this statement is supported by actual results on full-size deflection tests made carefully in the laboratory. In one case 4-in. channels were investigated, and in another 1-in. round cold-drawn shafting. In both series the physical properties of the open-hearth grades were considerably higher than the bessemer grades, yet the deflection results indicated the bessemer grades to be consistently from 5 to 10 per cent stiffer. Comparison of the deflection properties of 0.08 per cent carbon bessemer and 0.18 per cent carbon open-hearth steels in the form of light-weight beams revealed the bessemer steel to be 10 per cent stiffer. In general, deflection tests on various sizes of hot-rolled bars in bessemer and open-hearth equivalent grades indicated that bessemer steel usually runs from 5 to 15 per cent stiffer than open-hearth steel. In the cold-drawn condition this superiority is further increased. These are instances in which the sensitivity to the cold work of bending becomes a useful factor.

Another instance of superior stiffness of bessemer steel lies in its application as tin plate for can bodies. Here bessemer plate forms a more nearly perfect round body, free from paneling or fluting. The flanges are generally free from "mushrooming" (or rolling up). Under vacuum packing conditions and handling, a bessemer can body will resist distortion to a higher degree than one made of open-hearth steel.

We shall illustrate this quality of stiffness of bessemer plate as compared with open-hearth by tests showing the maximum load required in deflection of various gages of plates. The test pieces are cut $2\frac{1}{2}$ by $1\frac{3}{4}$ -in., with the long dimension parallel to the rolling direction. The span is about $2\frac{1}{8}$ in. and the load applied slowly by a flat bar about $\frac{1}{8}$ in. thick across the entire width of the piece. Fig. 1 shows a typical comparison.

In addition to its stiffness, bessemer steel has some advantage in tin-mill operations because of the lesser tendency of the sheets to stick together in hot mill rolling and subsequent annealing.

Many other examples could be given to illustrate the stiffness qualities of bessemer steel but those mentioned should suffice in indicating the superiority of bessemer steels in this field.

Weldability

A large outlet for bessemer steel lies in welded pipe. In this commodity the higher strength of low-carbon bessemer steel offers some advantage in a structural way over open-hearth. The machining quality being superior also, it is preferred for machining of threads. In welding quality it gives a good account of itself, the grain appearing closely

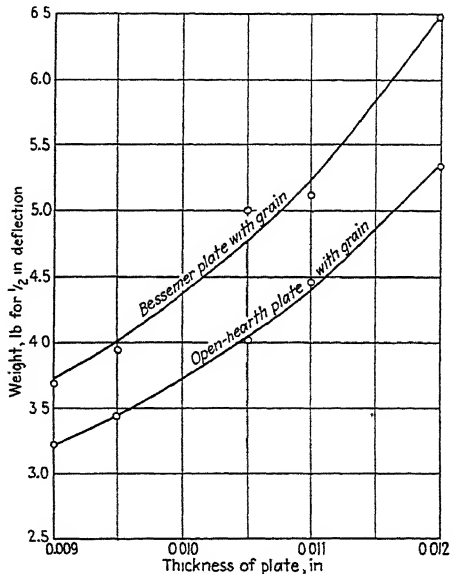


FIG. 1.—STIFFNESS OF TIN PLATE AS MEASURED BY WEIGHT REQUIRED FOR $\frac{1}{2}$ -INCH DEFLECTION.

knit and crystalline on fractures through the weld, whereas open-hearth steel shows a fibrous fracture with somewhat less indication of knitting. In manufacturing welded tubes the crop ends are crushed so as to open up at the weld for inspection. Some general idea of the comparative welding quality of bessemer with open-hearth steel may be obtained from the typical table of crush-test rejections on butt-weld tubes (Table 10). This

TABLE 10.—Crush-test Weld Rejections on Butt-weld Tubes

| Tube Size, In. | Bessemer Steel, Per Cent Rejected | Open-hearth Steel, Per Cent Rejected |
|----------------|-----------------------------------|--------------------------------------|
| 2 | 1.1 | 1.2 |
| $1\frac{1}{2}$ | 0.6 | 0.7 |
| 1 | 0.4 | 0.8 |
| $\frac{3}{4}$ | 0.2 | 1.8 |
| $\frac{1}{2}$ | 0.1 | 0.5 |

tabulation involves about 300,000 tubes and the results in general favor the bessemer steel. In addition, bessemer steel is distinctly superior from the standpoint of forming and rolling and consequently the final tube product is freer from scratches and roll marks.

A more severe test method applied in investigational work to determine the weld quality of welded tubing is the coiling test. This method involves coiling a tube cold around a mandrel of suitable diameter, depending upon the tube size being tested. Typical comparative results of open-hearth and bessemer steels are given in Table 11, which further substantiate the superior welding qualities of bessemer steel. The results definitely favor bessemer steel in this test.

TABLE 11.—*Coiling-test Failures*

| Tube Size, In. | Mandrel Size, In. | Bessemer Steel | | Open-hearth Steel | |
|----------------|-------------------|-----------------|-----------------|-------------------|-----------------|
| | | Number of Tests | Per Cent Failed | Number of Test | Per Cent Failed |
| ½ to 1¼ | 3½ to 8½ | 606 | Normal | 631 | 13.2 higher |

In addition to tubing, the welding characteristics of bessemer steel are utilized in fairly large tonnages for axe poll where it is successfully welded to open hearth axe bits. These and similar applications favorable to bessemer steel constitute an inherent commercial advantage of the process.

Sensitivity

It has long been recognized that bessemer steel shows a more pronounced reaction to cold work than steel made by any other process. This feature has commonly been considered an unfavorable characteristic under more or less all circumstances. In very recent years, however, a much clearer understanding is being arrived at with respect to embrittlement and associated phenomena; and it is now recognized that a sharp reaction to cold work may be either a favorable or an unfavorable characteristic when intelligently viewed in the light of the requirements of a particular application. This better understanding has resulted in more accurate application of bessemer steel to uses where it is superior to other grades, with a general enhancement of reputation for this steel in its own field.

An example of the susceptibility of bessemer steel to cold work is shown by the results in Table 12, which represent a bar of bessemer screw steel subjected to various drafts in cold-drawing. These results indicate the desirable increase in the yield point and tensile strength that can be accomplished within the range of commercial cold-drawing practices. While the yield and tensile strength have been progressively increased greatly, yet a good degree of ductility is maintained.

TABLE 12.—*Effect of Increased Cold Work on the Physical Properties of Bessemer Screw Steel*

| Size, In., Hex. | Cold-work, Per Cent | Yield Point, Lb. per Sq. In. | Tensile Strength, Lb. per Sq. In. | Elongation, Per Cent in 2 In. | Reduction, Per Cent |
|-----------------|------------------------|---------------------------------|--------------------------------------|-------------------------------------|------------------------|
| $\frac{1}{2}$ | None | 42,310 | 65,740 | 28.2 | 60.6 |
| $1\frac{5}{16}$ | 12.4 | 86,170 | 91,200 | 18.0 | 56.0 |
| $\frac{1}{4}$ | 23.6 | 96,120 | 102,400 | 12.0 | 43.0 |

The difference in the effect of cold work upon bessemer steel and equivalent tensile open-hearth steel on the same size bar, and subjected to the same cold-drawing process, is indicated in Table 13. The yield points in this case were determined by the extensometer method and the results are the averages of four tests. While the tensile strength was about the same in the hot-rolled condition, cold-drawing increased the yield point about 19.0 per cent and the tensile 13.0 per cent more than was accomplished on the open-hearth grade. This difference in the reaction to cold work is typical and is considered a favorable factor for obtaining maximum physical properties in many applications. When this sharp reaction to cold work is not desired it is possible to modify this characteristic through the medium of special deoxidation, as now practiced almost generally in the manufacture of open-hearth steels.

TABLE 13.—*Comparison of the Effect of Cold Work on Bessemer vs. Open-hearth Steel*

| | Bessemer Steel | | Open-hearth Steel | |
|-------------------------------------|----------------|------------|-------------------|------------|
| | Hot-rolled | Cold-drawn | Hot-rolled | Cold-drawn |
| Yield point, lb. per sq. in. | 42,780 | 75,040 | 39,040 | 63,220 |
| Tensile strength, lb. per sq. in. . | 64,900 | 88,170 | 65,000 | 77,880 |
| Elongation, per cent in 2 in. | 38.0 | 19.5 | 36.5 | 19.0 |
| Reduction, per cent. | 65.2 | 53.3 | 61.8 | 57.0 |

GRAIN SIZE

The application of various steelmaking practices to bessemer steel in order to control grain size has been studied. Any large measure of control is attended with some difficulty because of the natural tendencies of bessemer steel to retain more nonmetallic matter, which constitutes nuclei for grain formation. In general it may be said that bessemer steels are fine grained and fairly resistant to grain growth. Usually they are abnormal and vary considerably in grain size under McQuaid-Ehn test. In some slighter degree their grain size may be influenced by manganese and aluminum as now practiced in grain-size control of open-hearth steels. Bessemer steels are not heat-treated to the same extent as open-

hearth steels, except possibly bessemer screw steel, which is carburized and heat-treated in the manufacture of many small parts. In spite of its usual abnormality and high sulfur content, it makes an acceptable grade for use when extreme ductility of core is not essential.

CORROSION (ATMOSPHERIC)

It is a recognized fact that the addition of 0.20 per cent copper minimum to carbon steel will greatly improve its resistance to atmospheric corrosion, thereby increasing the useful service life by about two to four times. Copper-bearing bessemer steel, that is bessemer steel with copper 0.20 per cent minimum, has fully demonstrated its capacity to resist atmospheric corrosion at least equally as well as the open-hearth copper-bearing steels. In fact, there are indications that point to a superiority for the bessemer copper-bearing steels.

The exposure results contained in the annual report of committee A-5 of the A.S.T.M. on Corrosion of Iron and Steel printed in 1928 included the final findings on sheets exposed at Pittsburgh and Fort Sheridan. While this test was primarily a comparison between copper-bearing and non-copper-bearing steels, a review of the results on the copper-bearing steels indicates the additional fact that the bessemer copper-bearing steels gave excellent results and in general appear to be substantially superior to the basic open-hearth steels. Table 14 gives a brief comparison of the committee's findings on the 22-gage sheets representing the bessemer and basic open-hearth copper-bearing steels.

TABLE 14.—*Corrosion Results on Bessemer and Basic Open-hearth Copper-bearing Sheet*

| | Fort Sheridan | | Pittsburgh | |
|-------------------------------|---------------|-------------|------------|-------------|
| | Bessemer | Open-hearth | Bessemer | Open-hearth |
| Months of exposure..... | 132 | 132 | 75 | 75 |
| Number of sheets exposed..... | 33 | 47 | 23 | 58 |
| Number of sheets failed..... | 0 | 10 | 5 | 58 |
| Percentage failed..... | 0.0 | 21.3 | 21.7 | 100.0 |

The comparisons are based on locations. In the Fort Sheridan exposure there were no failures in the bessemer while 21.3 per cent of the open-hearth sheets failed. In the Pittsburgh location, where the atmospheric conditions were more severe, 21.7 per cent of the bessemer sheets failed, compared to 100 per cent failure of the open-hearth sheets.

A similar condition is revealed in a privately conducted test of 3-in. welded tubing exposed to the weather on the roof of an office building in Pittsburgh. This test has been exposed for a period of 60 months and examinations so far made have revealed a weight loss of 2.41 per cent for

the low-carbon copper-bearing bessemer steel as compared to a weight loss of 7.83 per cent for the low-carbon copper-bearing open-hearth steel. From the trend of the results, it seems likely that the corrosion differential between the two steels will be maintained as the experiment proceeds.

In view of the favorable evidence pointing to the superior resistance to corrosion for copper-bearing bessemer steel in steel products exposed to the weather, it would seem that a wider commercial application is justified, and that this practical phase should receive increased attention.

CONCLUSIONS

Any steelmaking process that possesses the unique quality characteristics plus operating flexibility that is embodied in the bessemer mill certainly deserves study and development. This appears to be especially true, since during the past five years the progress made in improving the quality of bessemer screw steel has demonstrated thoroughly what might be accomplished through the application of adequate metallurgical effort.

The extent of further possible development will depend entirely on the amount of technical attention applied. It seems reasonable to predict that other desirable inherent quality characteristics of the bessemer process can be developed and improved for further commercial application, as has been done for bessemer screw steel.

This paper has been written from the point of view of bringing out the positive characteristics of the bessemer process, as it is believed that the deficiencies of bessemer steel are well known and probably often over-emphasized. In a brief way the paper has reviewed manufacturing methods, operating practice and certain quality characteristics of bessemer steel, showing typical data illustrating the results obtainable under various comparable phases.

These illustrate the possibilities of development of present operating practice as well as greater control of the ultimate quality of bessemer steel. If they serve to generate interest or development from the standpoint of either steel producer or consumer they will have served a purpose that ultimately should benefit both.

ACKNOWLEDGMENT

The writer wishes to express appreciation for the assistance of his various associates in preparing this paper.

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DISCUSSION

(*Eric R. Jette presiding*)

G. B. WATERHOUSE,* Cambridge, Mass.—I am interested in the use of pyrites as compared with either stick sulfur or flours of sulfur. Our experience was diametrically opposed to Mr. Henning's. We found that stick sulfur in the ladle gave far better results. I should like to know at what stage of the operation the pyrites are added to the vessel.

C. C. HENNING.—Pyrites were added in the charge.

H. D. HIBBARD,† Plainfield, N. J.—The Riverside Iron Works at Benwood, W. Va., about 1883, started a bessemer mill to make nail plate for cut nails. The development of the wire nail about 1888 led to the abandonment of the cut nail, and the company had this bessemer plant on its hands; so, looking around for something to do with it, Mr. Hearn, who was general manager, decided on welded pipe, and put in a pipe mill. They made bessemer steel, rolled it into skelp, made pipe of it and it welded beautifully. That they had the best process to give weldable steel was pure luck. Its resistance to corrosion was another matter.

It was remarkable how that pipe stood the tests that had been given to wrought-iron pipes. One of the tests was to fill a piece of pipe with water and expose it to freezing temperature. While all iron pipes tested in that way split, the steel pipe did not. No one could understand why, that was until the pipe was measured, which indicated that it had stretched enough to allow the ice inside to expand.

This property of weldability of bessemer steel has never been explained, so far as I know but it has never been equaled by steel of any other kind. The open hearth cannot make steel that will weld as this bessemer steel will.

A friend of mine in Scotland who made pipe told me about this weldability of American bessemer steel. He said, "We can buy a lot of American steel and it will weld 100 per cent." He did not qualify that. That was the situation in that particular factory when the price of American bessemer steel went above the price at which steel could be bought from the European continent. Because of the increased price, they stopped using it. They got stuff that would weld fairly well but not as well as the American steel. I was in that mill some time afterward and the mill foreman, speaking about that, said, "Yes, I have 11 pieces of American skelp here I will show you." He got them in and made 11 pieces of good pipe. I should like to know why bessemer steel will weld so much better than open-hearth steel of the same composition, as far as the chemist is able to tell us.

C. C. HENNING (written discussion).—Mr. Hibbard's comments on the superior weldability of bessemer steel serve to confirm our own views and experience. The reasons for this superior welding quality over open-hearth steel are not definitely established. One view would be that oxygen may be a factor. In the operation of the bessemer, a uniformity of oxidation is almost essential. This, in turn, induces a "wetness" of the heated steel surface that permits a higher degree of penetration of the skelp edges. Another view is that the comparatively high phosphorus of bessemer steel is a factor favoring weldability.

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A Chemical Engineer Views the Steel Industry

BY CHARLES F. RAMSEYER,* MEMBER A.I.M.E.

(New York Meeting, February, 1935)

THE manufacture of iron and steel is one of the largest of our industries; and in point of size of single plant and equipment certainly the biggest of all industries. By the general public it is generally considered a prime example both of the marvelous technical advances achieved by modern science and engineering in the design and operation of equipment and of the efficiency of big business in the coordination of men and materials. Actually the operation of its basic processes has not changed significantly in either theory or fundamental design of equipment in the past 75 years. Though many other process industries have been born and developed, and not seldom completely revolutionized, during this period, the primary processes of making iron and steel are still carried out along the lines laid down, and in the equipment originated so long ago, by Bessemer, Siemens and Martin, and subsequently expanded to practically the modern scale by Carnegie, Schwab and Captain Bill Jones in the eighteen eighties and nineties. The application of the principles underlying the continuous counter-current physical and chemical interaction of solids, liquids and gases, which have been so successfully used in the rapid evolution of our chemical process industries, has been very largely lacking in the steel industry.

In the days of the last-named giants, especially, Carnegie, the steel industry made great and rapid technical progress. Carnegie's ever driving idea (as later with Ford in the production of automobiles) was the finding of new and better ways of making cheaper steel. Carnegie himself was a steelman, and so long as he dominated the industry its technical progress was rapid; and he, like Ford, was vastly successful financially as well, since his costs were continually being driven lower than those of his competitors by his advances in steelmaking technique.

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By the beginning of the twentieth century, however, the industry had grown so large that no one man's personal interest in its technical development was sufficient to divert its attention very far from the main business in hand, that of making money for its new owners, or at least for its controlling group of financiers. The general policy of the industry seemed to be to make as much money as possible, with as little risk as possible, and in this "direct" pursuit of profit the search for improved processes languished. Changes were almost entirely confined to minor improvements in construction and the routine details of operation along lines already laid down. Such new things as there might be were either still-born or died of exposure before they had gained strength. With the growth of the country and the demand for steel, plants grew larger to conform to the size of the units in them, electricity was substituted for steam, and in mechanical ways, especially in the handling of material, a field in which America excels the world, the industry grew more efficient; but its process equipment remained fundamentally the same in design as it had been for two generations.

While automobiles were being made better and cheaper with ever newer processes—a feature of that industry which has persisted up to the present time—tonnage steel, as distinguished from the special and alloy steels, grew neither better nor cheaper. While the oil industry went from batch to continuous processes and cut refining costs in two, steel continued to be made in the old-fashioned way, increasingly in the open hearth. (The open hearth is a batch furnace for melting and refining steel akin in principle to heating water by first pouring it into a saucer and then holding a candle flame close to its surface, except that with steel the additional precaution is taken of carefully covering it with a nice thick layer of slag, which effectively protects it from taking up heat efficiently.)

CAUSES FOR LACK OF DEVELOPMENT

Just why the steel industry failed to continue its early prodigious strides in process development is hard to explain. There are many possible reasons. Its long hours and hard life perhaps kept some of the more imaginative young engineers from its plants. Operating executives of exceptional intelligence and ability who rose to be officers of their companies were usually quick to see upon arriving in New York that they could make much more money in Wall Street than they could ever hope to obtain by developing new and better methods of making steel for their companies. The continued growth of the country and its demand for steel supplied sufficient profits so that competition was not too keen and there was no great urge to do much better. The non-technical bankers, lawyers and financiers at the heads of the larger companies were against spending large sums on dubious experiments,

and when they did attempt some experimentation they were frequently ill-advised and unsuccessful. From sad experience they learned how expensive high-temperature metallurgical development work could be, and they were loath to experiment in a field where millions were required to prove out new ideas. Their choice of operating executives naturally favored men who had made low cost records, generally by avoiding all experimental expenditures and sticking to proved methods and equipment, as good operating men should do. Perhaps, too, the tremendous investment in plant made them apprehensive of the financial dangers of sudden obsolescence. The more highly trained technical men with time to think became largely fascinated by the new alloy steels, to the exclusion of other interests, though such steels represented, and still do, but a small part of the total steel tonnage produced; and the plants continued to be run largely by the more conservative operating men along the old lines. Moreover, no one of the larger companies was wholly owned and controlled by a single individual or small group, and none, even though it had the initiative and resources, could spend money on a large-scale process development without having to listen to the demands of its stockholders for dividends. Probably all these factors had something to do with the situation. But whatever the cause, the result was and has continued to be a complete lack of any important new developments in the making of the ordinary tonnage steels, which amount to 90 per cent or more of the industry's total production.

THE STEEL INDUSTRY

Steel is a highly vertically integrated industry, the same company ordinarily mining its own ore, limestone and coal, frequently operating its own steamships and even railroads, making its own coke and smelting its own pig iron, which, with more or less steel scrap, is finally turned into the various finished steel products made by a "steel" company. In mining and transportation, and even in cokemaking (a highly developed art), progress has not been dependent on the steel companies alone, since these operations are common to other industries as well, and in these fields the steel companies are, if not right up to the times, at least not very far behind. It is in the blast furnace and steel plant itself, in the conduct of the processes peculiar to their own industry, that the steel companies have failed to advance in the past 45 or even 75 years, in step with the revolutionary changes that have taken place in other process industries.

The molten pig iron produced by melting iron ore, limestone and coke together in a blast furnace is subsequently turned into steel in the open-hearth furnace, from which it is tapped into ladles for pouring into molds. The contents of these molds form steel ingots. The rolling mills work these ingots into steel products ranging from railroad

rails and structural beams to tinplate (for cans) and wire (for hairpins). It is with these processes and their failure to show much change during the present century that we are concerned, especially with the making of steel in the open-hearth furnace. The blast furnaces and the rolling mills, particularly in the final rolling of small products, are the more highly developed, but even in these two more progressive departments development has been along conventional lines; refinements in detail rather than fundamental changes. While the bulk of our criticism therefore will be directed against the open hearth—that is, the steelmaking and refining process proper—we will endeavor to make our discussion somewhat more complete by considering all three operations in order, starting with the blast furnace.

THE BLAST FURNACE

Since a large part of blast-furnace operation resolves itself into a question of material handling, we should expect to find that this phase of blast-furnace operation is usually well worked out; and so, in fact, it is. Furthermore, the blast furnace has an added advantage as a process in that as originally developed it was based on the technically sound principle of the counter-current utilization of both heat and materials; so that early it was discovered to be thermally the most efficient of all steel-plant furnaces, and it still remains so. In spite of this advantage there are a few things about blast-furnace operation that seem a bit strange to the outsider.

The first anomaly in blast-furnace operation is that despite a complete unanimity of opinion among blast-furnace men that the secret of successful operation is uniformity and regularity in the flow of materials to and from the furnace, no attempt has been made to remove the iron and slag from the furnace continuously. The water that collects in the blast-furnace gas mains drains itself off continually through water seals, but no effort to remove the molten iron from the furnace similarly through a liquid "iron seal" has been made, though the advantages of such a constant knowledge of the quality of the product would be manifold.

Large sums are spent on the construction of huge regenerative checker chambers, called blast-furnace stoves, of which each furnace usually has three or four, for preheating the air blast of the furnace, and yet ordinarily they are run far below capacity in order to have available at all times a reserve of heat to be used in case of need to control the temperature in the lower part of the furnace. Would it not be more sensible to use these expensive pieces of equipment at their highest efficiency and capacity at all times, and control the furnace temperature by adding a little extra heat directly to the hearth in the form of addi-

tional fuel as required? Yet no comprehensive experimental work is being done along this line, so far as is known, in this country.

OXYGEN FOR COMBUSTION

Another and much larger field for development in blast-furnace work is the use of oxygen instead of air for combustion. Much has been written on the subject but very little done. The practical man usually has gone into it no further than to inquire whether equipment is available to produce the tremendous volume of oxygen required by a blast furnace, and how much it would cost, and upon finding the cost apparently prohibitive has dropped the subject. But it has many possibilities. For one thing, it would greatly increase the capacity of a given furnace, and since the steel code does not permit the building of new furnaces, this may turn out to be of importance for some growing company.

It is not commonly realized that most of the present equipment could be used for oxygen without alteration by the recirculation of the top gas from the furnace with added oxygen until all nitrogen was worked out of the system. The gas-engine generators and blowing engines running on a gas-oxygen mixture would exhaust at blast pressure into the blast mains, thus increasing the blowing capacity, and the oxygen would be added to the blast either before or afterward to form a blast gas containing solely carbon dioxide (instead of nitrogen) and oxygen. Furnace temperature would be controlled by varying this ratio, the stoves being run at capacity at all times. The top gas would have more than twice the heating value of the present blast-furnace gas, assuming the same ratio of carbon monoxide to carbon dioxide, thus providing all the heating gas necessary for all other operations of the steel plant. The energy-carrying capacity of all blast-furnace gas mains would likewise be doubled. Since the process outlined would entail primarily the substitution of a mixture of carbon dioxide and oxygen for the nitrogen in the blast, the blast volumes and other conditions would not change radically, and most of the present equipment could continue in use.

A proposal that offers so many advantages is well worth a searching and detailed study. The theoretical power required to produce oxygen from the air is low, and would be furnished in large measure by the present blowing engines, using the energy that now is required to compress the nitrogen in the air. Much development work would have to be done, especially on the oxygen end, but the steel companies can hardly expect the liquid-air companies to do it without more encouragement than they have received heretofore.

Another and increasingly troublesome problem with most blast-furnace plants, especially those close to urban centers, is the disposal of the slag, of which from $\frac{1}{2}$ to 1 ton or more accompanies the production of each ton of pig iron. With the furnace temperatures available with

the use of an oxygenated blast it should be possible to solve this problem, at least for many types of pig iron, by increasing the lime content of the slag to the point where it could be ground directly for the production of portland cement. The blast-furnace operating man will reply at once that this cannot be done. But this has not been proved because no one has yet intelligently tackled the problem with adequate backing in a serious attempt to solve it. Development work cannot be done effectively by people with regular operating duties, as has long been recognized in our more profitable industries, but not as yet by most steel companies. If any such work is done at all in the steel plant, it is usually done by the department superintendents in their spare time.

THE OPEN HEARTH

When Siemens conceived the idea of the double regenerative furnace for obtaining high temperatures—that is, the preheating of both gas and air before combustion—and applied it to the remelting of steel scrap, it was a tremendous advance over anything that had been known before. But that was 75 years ago, and to the uninitiate, not observing details too closely, Siemens' original open-hearth furnace and a modern one look so much alike as hardly to be told apart. It would probably be hard to find another industry in which the man of 1860 would recognize present-day equipment so easily.

In considering the process of turning steel scrap and pig iron into finished steel as primarily a problem in heat transfer and chemical reaction, we can begin by asking just what an open-hearth furnace attempts to do. Primarily, its functions are to remelt steel and pig iron, if the latter is not received molten, and then to purify the mixture into steel by oxidizing its impurities and absorbing them in the slag. The three objects of the open hearth are: (1) melting, (2) treating the molten mass with a purifying liquid—the slag, and (3) finally separating the two. It accomplishes these objects by blowing down a flame on top of the metal to melt it and the slag materials, and then allowing the slag that is lying on top of the molten metal to react slowly with it. The minute nonmetallic (slag) impurities in the metal rise slowly to the top, being lighter than the steel (just as dirt slowly settles out of muddied water). This inefficient method of heating two substances and letting them react without any positive method of mixing them, or of separating them after the reactions are complete, keeps even the best open-hearth furnaces from melting more than 300 tons or so of steel in a day, at a thermal efficiency of 10 to 15 per cent, while a blast furnace can develop three or four times as much heat with an efficiency fourfold to fivefold greater. The fundamental difference is that a shaft furnace—such as a blast furnace—operates both thermally and chemically on the counter-

current principle, while an open-hearth furnace is but a batch kettle, and an extremely inefficient one in the bargain.

There is no intrinsic reason why steel scrap should not be melted in an oxidizing blast furnace fired with oil or pulverized fuel, whereby the tremendous advantage of using a shaft furnace would be obtained. A single furnace of that kind the size of a normal blast furnace would have a scrap-melting capacity equivalent to a score of open-hearth furnaces, and it should cost only two or three times as much as one of the latter. Whole automobiles could be run into the top of such a furnace without any pressing or scrap-bailing operation, and run out at the bottom a few hours later in the form of liquid steel scrap ready to be converted into high-grade steel, either by mixing and refining with molten pig iron or with carbon by itself. This would dispose of the first function of the open-hearth furnace—the melting of the scrap.

Oxidizing Impurities

The second major function in steelmaking that takes place in the open-hearth furnace is the oxidizing of the impurities of the charge and their elimination by absorption in the slag. As a means of forwarding the chemical reaction between the two materials by mixing, it would be hard to devise a more inefficient apparatus than the open hearth. In the first place, the metal must be kept molten by the heat from the flame, which can only reach it by passage through the slag, which is more of a heat insulator than a conductor; in the second, instead of the two reacting substances being intimately mixed in a state of violent agitation, as they should be, one lies more or less quietly on top of the other, the only contact between them being the single flat and relatively quiet interface. At the temperature of molten steel, the purifying reactions between slag and metal are almost instantaneous if the slag and metal are brought properly into contact with each other; but no use is made of this well-known fact. The open hearth takes hours to do what the bessemer, by intimate mixing and violent agitation, does in 10 minutes. There is no fundamental reason why the oxidizing basic open-hearth reaction between slag and metal should not be similarly speeded up; nor, to go a step farther, is there any reason why the bessemer process, which is a great improvement as far as it goes, should not be made continuous instead of intermittent.

We have already seen that the steel-scrap melting function of the open hearth may be performed with quadrupled economy in an oxidizing shaft blast furnace. Why not do the same thing for the slag, either in the same shaft with the scrap or in a separate smaller slag-melting oxidizing shaft furnace? Here again there would be the advantage of the vastly greater thermal efficiency of continuous shaft melting as compared with batch heating.

Mixing and Separation

With molten steel scrap, molten pig iron and molten basic oxidizing slag at hand, all produced continuously and uniformly at a constant predetermined rate in the most efficient possible manner, all that is left to do is to devise equipment that will mix the three together thoroughly, allow them to react, and then separate the mixture, in order to produce steel with but a fraction of the heat, capital investment and labor required by the conventional open-hearth process. The mixing of the three must be carried out continuously, not by any batch process; but this does not seem very difficult in view of the fact that molten steel is two or three times as heavy as molten slag. It certainly should not be impossible to devise a slag tower or column through which to drop the steel in a finely divided state, and to collect the metal at the bottom. This has already been done in part by Aston in his brilliant and revolutionary process for the production of wrought iron, which is now in actual commercial operation—the sole significant development in ferrous metallurgy since the Civil War! The purifying-column process should be carried on in a counter-current manner, after the best practice of the chemical process industries; the nearly used up slag meeting the most impure metal, while the nearly purified metal finally separates from the freshest slag. This would have the great advantage of decreasing the amount of slag necessary per ton of steel, and in the basic process would raise the phosphorus content of the spent slag high enough to enable its sale as a fertilizer, as is done with basic bessemer (Thomas) slag abroad.

Elimination of Dirt

We now have a chemically purified steel, continuously produced, with the utmost regard for economy of fuel and materials, simply by utilizing the known efficiency of shaft furnaces and the counter-current treatment of the hot molten steel-pig mixture as it falls through a rising column of slag. The only function of the open-hearth furnace not discussed is the elimination of the nonmetallic impurities; i.e., oxides or "dirt," left in the steel, which will necessarily be left over from the rapid and efficient, though violent processing to which we have subjected our steel.

The elimination of the dirt should not be difficult if we do not allow ourselves to be bound by the limitations of conventional practice. What do other industries do when they have a liquid contaminated by small amounts of other nonmiscible liquids or solids? The filter press is out of the question; the particles are too finely divided and there are no materials of which to construct a filter. But what of the separation of milk and cream or water and oil? They differ in density by very small percentages, while the dirt in steel is less than one-half as heavy as the

metal in which it is suspended. With this advantage of a much greater difference in density, the centrifugal separation of the steel from its suspended impurities should be simplified. All that is needed is some man of the caliber of Captain Bill Jones, and the deed will be as good as done—and probably made into a continuous process as well. Has any steel company ever seriously (to the extent of a million dollars) proposed a joint investigation for the development of such a machine to a leading manufacturer of centrifugal separators? We doubt it.

There are other treatments that might well be applied to steel; for example, passing it through a reducing slag to further purify it, and subjecting it to a vacuum to draw off the dissolved gases, which frequently cause a lack of soundness (blowholes) in the final product. This development has already taken place on a small scale in some countries, and the outsider marvels that more has not been done with it. A number of simple methods of applying the principle in practice will immediately suggest themselves to almost anyone. If nothing better can be devised, let the whole casting process take place in a vacuum. Anyone familiar with the size of the huge vacuum chambers on the condensers of a large modern steam turbine—big enough to hold a small cottage—can easily visualize such a process. This development may well be one of the first of the suggested possibilities to materialize. Even the five thousand year old clay industry has started to vacuum-treat its raw material within the past few years.

To sum up, the open-hearth furnace is a most inefficient melting and mixing unit, and even as a settling chamber leaves much to be desired in the way of capacity. Too much time is required to let steel purify itself by just sitting still—no modern process industry would tolerate such a tedious method for a moment. So we may as well agree to its eventual abandonment. Such an irrational piece of equipment cannot hope to live forever merely because its builders and operators are too lazy to make a change. The change will be forced on them.

THE FORMING OF SOLID STEEL

In the finishing mills there is little to quarrel with. Americans are mechanically inclined and the smaller shape and section mills are marvels of mechanical ingenuity, running almost automatically at tremendous speeds and high capacities. To anyone watching the flashing loops of hot steel, sometimes traveling over a mile a minute, through the repeaters and finishing rolls of a modern wire-rod mill, it would seem that the zenith of mechanical perfection had been reached. A visitor sees a mill hundreds of feet long with scarcely an operator visible except in times of trouble. There is little point in criticizing something that seems to come so close to the ultimate in efficiency.

But it is still possible to be critical about the turning of liquid into solid steel, accomplished by casting the molten metal into huge ingots which cool so slowly that the originally homogeneous liquid metal is far from homogeneous by the time it has solidified. The extremely slow cooling of the mass causes the development of a large, weak, crystal structure which is only partially removed in the rolling process. Segregation of impurities and the shrinkage of freezing and cooling force the discard in the blooming mill up to 30 per cent of the weight of the ingots as rolled. This can hardly be called efficient. It is well known that the most favorable physical structure in steel is that produced by chilling it rapidly in small sections. Why not do it continuously? If Henry Ford could show the world how to make plate glass from a continuous stream of the molten raw material, is it not at least conceivable that the same thing could be done with steel? A vastly different technique might be required, to be sure, but there is no reason to believe that insuperable obstacles would be encountered. It is purely a problem in mechanics, materials and the flow of heat, and without question would yield to an intelligent attack. Ten years? Perhaps, but that is a short time to spend on a process capable of producing such tremendous savings. Nor need we limit ourselves to the continuous formation of steel plates. All small shapes and reasonably thin sections, up to an inch or so in thickness, should be amenable to continuous casting treatment. With the metals of lower melting points satisfactory experimental results have already been obtained. Let us hope that some day the blooming mill will be relegated to rolling finished heavy products and be no longer retained as a means of partly correcting the defects inherent in the present process of casting steel into ingots. To pour homogeneous molten steel into huge ingots only to roll them down again into smaller pieces containing imperfections, of which most can be traced back to the casting and freezing of the ingot, is absurd.

COST OF RESEARCH AND ITS REWARDS

Thus an outsider looking at the steel industry sees antiquated processes and methods based on ancient and insufficient assumptions as to the limitations of equipment and materials, being driven by the latest type of electric motors and controlled by the most modern instrumental devices. A strange commentary on the inconsistencies of the human mind.

Even though much of the lack of technical progress in the steel industry may justly be laid at their door, all this stagnation in process development cannot and should not be blamed solely upon those in control of the steel companies of the world. High-temperature experimental and development work on a large scale is extremely expensive. Small-scale operation is not easily possible with molten materials that solidify in an instant when anything goes wrong, so that units at least

half the usual size must be built if one is to proceed with any assurance of success. Refractories on a small scale fail at points that could be protected or replaced by water cooling on larger equipment without danger of freezing up the whole reaction. For every hundred thousand dollars spent on the trial of chemical processes on a semicommercial scale (and there are many) a million dollars might easily be required in the high-temperature field. Sums of this magnitude are not available for experimental work by any but the largest companies, which more often than not are quite content to let someone else do the pioneering.

The price is high, but the rewards are great. How great is not often realized; if it were, perhaps more interest would be shown by the steel companies in starting a serious study, if only on paper, of some of the more immediately realizable possibilities in process development. Their own technical staffs tend largely to accept the immemorial practices of their plants as they find them; in which attitude they are doubtless encouraged by the millmen themselves. Discussion of revolutionary changes is actively discouraged by many responsible operating executives as chasing after rainbows. For this reason the managements of some of the more advanced industries do not believe that the burden of technical progress can properly be placed upon the shoulders of the operating man. If we are to believe them, we must then disbelieve the operator's glib assurance that some new idea is not "practical." Experiment, not discussion, should decide the issue. There is much truth in Arthur D. Little's remark that "with monotonous repetition the new has been rejected by those presumably best qualified to appraise its worth." No one can deny that the research staffs of the steel companies have turned out a vast amount of good fundamental theoretical work, but little of it has ever been applied to the development of practical equipment problems. Special steels, forming but a small percentage of their total output, tend to be studied to the exclusion of any new process development work on the production of the ordinary tonnage steels, which constitute nine-tenths of their total manufactures and on which a saving of a dollar a ton would yield truly fabulous returns.

AN IDEAL PLANT

Let us consider an ideal plant of the future and hazard a guess as to the savings that might be made with it. We will start with two blast furnaces, making 2000 tons of pig iron and 1000 tons of portland cement clinker per day, besides supplying gas for all other heating purposes. Add to this a small oxidizing shaft furnace for melting 2000 tons of miscellaneous scrap a day—"heavy melting scrap" would have no special significance for such a furnace. Add also a still smaller one melting 100 tons of oxidizing slag, sold for the fertilizer value of the phosphorus it has taken out of the pig iron. The molten steel scrap and

pig thus produced will be fed continuously down through a rising body of the oxidizing slag and drawn off through a liquid metal seal at the bottom for centrifugal, vacuum, or other special treatment before going to the continuous-molten-to-solid-metal casting tank or mixer, from which the hot, solid, endless bar or shape issues and is "finished" rolled to size without the production of scrap. This is no wild phantasy. Half the details have already been worked out in other plants or processes, either for steel or other materials. To work out the rest of the problem would require merely time, money and technical imagination.

In such a plant, the open-hearth shop would be replaced by an investment of less than half as much; ingots and blooming mills eliminated altogether; the production of mill scrap reduced by 90 per cent; one-third to one-half the present fuel requirements saved; not to mention a profit of a dollar or two a ton on the basic refining slag (fertilizer) and another dollar a ton on the blast-furnace slag (cement clinker). Such a plant, I believe, when smoothly functioning, would show a saving in the cost of steel of at least \$5 a ton.

It can be done. The chemical process industries have demonstrated the correctness of the fundamentals, and steelmaking is essentially a chemical process. All that is required is the will and the money. Though development work on the whole project when well under way might easily cost \$5,000,000 a year over a period of 10 years, or a total expenditure of \$50,000,000, the saving at \$5 a ton in this country alone on a production of but 30,000,000 tons of steel per year, would give an annual saving of \$150,000,000, or 300 per cent on the investment. This return from process development on the "tonnage" steels is far greater than can possibly be realized from the special alloy-steel development and production-control work in which most steel-mill metallurgists are engaged at present.

How or when or whether anyone or any group will try to develop the production of steel in this way, along the lines followed so successfully in the chemical process industries, is an open question. One may well doubt whether there are men in the steel industry in this country with the money, power and technical imagination to drive such a scheme through to practical completion. They would have to be giants, and perhaps the day of giants in the steel industry has passed.

The new industrial codes may help. The emphatic "No" of the code authority to some progressive company's request for additional open-hearth capacity may furnish a sufficient incentive for the development of a new steelmaking process. On the other hand, perhaps the only place where there is enough energy, enthusiasm and lack of respect for precedent to make such an undertaking possible is in the new and growing steel industry in Russia, destined some day, from the size of the country, the extent of its resources, and a constantly increasing demand, to be as

great as our own steel industry has become under similar conditions during the past 75 years.

To those steelmen who shout, "Impracticable dreams!" we can but repeat Dr. Little's remark on the history of technical development: ". . . with monotonous repetition the new has been rejected by those presumably best qualified to appraise its worth."

DISCUSSION

(Francis L. Toy presiding)

G. B. WATERHOUSE,* Cambridge, Mass.—I should like to give a little background of this paper. Mr. Ramseyer is a graduate of our Institute, in chemical engineering. He took a cooperative course, which means that he had to go to various stations. One of these was the Lackawanna Steel Co., in Buffalo; there he studied the plant from the chemical engineering standpoint, but became familiar with the steel business to a large extent. At the Institute he took a number of courses in iron and steel. After he took his Master's degree, he worked in the blast-furnace department of the Illinois Steel Co. for some years. So while he calls himself a chemical engineer, he really has a good deal of the iron and steel background. He has had in mind for a good many years the ideas expressed in his paper and finally was persuaded to put them in writing.

R. H. SWEETSER,† New York, N. Y. (written discussion).—Mr. Ramseyer's thought-provoking paper on his views of the steel industry is characteristic of a man who has had a blast-furnace training; it is said that "a blast-furnace man tells the truth but not all the truth." If all the research work that has been done at blast furnaces and steel plants were published it would reveal that large sums of money, much time, thought and energy have been expended in attempts to find better and cheaper ways to make iron and steel; a great deal more of such research work has been done than is indicated by Mr. Ramseyer's paper. None of us likes to report failures, although it is very important that negative results should be recorded.

On the other hand, I agree with Mr. Ramseyer that the steel industry has failed "to continue its early prodigious strides in process development." The reasons he gives for this failure seem to cover the ground, especially when he says, "the nontechnical bankers, lawyers and financiers at the heads of the larger companies were against spending large sums in dubious experiments, and when they did attempt some experimentation they were frequently ill-advised and unsuccessful." Some of the smaller companies were wise enough to venture into the regions of untried processes and became successful.

I doubt whether there is a steel company in America that does not have one or more skeletons of experimental failure of more or less impractical ideas. While I was superintendent of a blast-furnace plant the president of the company had a long list of seemingly foolish tests that he wanted made. So many of them had failed that I was getting skeptical, but he remarked one day that if he found one success out of a hundred ideas it was worth while. The results of the searching work of that wise ironmaster, the late Col. John Gordon Battelle, are now being perpetuated in the Battelle Memorial Institute.

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† Consulting Engineer.

One outstanding instance of wisdom happened several years ago in a smaller blast-furnace company that later became part of one of the most successful of the steel companies. In comparing costs of pig iron, two executives found that one company had controllable costs (the cost above the cost of materials) nearly double those of the other company. The high-cost executive asked why that was so and the other man said, "Because you are not a blast-furnace man." He replied, "Well, I can change that situation." And he did; he resigned, and put in a man who was blast-furnace-minded and after that his costs were more nearly ideal.

It is true that "development work cannot be done efficiently by people with regular operating duties." Mr. Ramseyer says that this fact has not been recognized by most steel companies. On the other hand, a regular research department is not sufficient to accomplish all that is necessary for progress in the steel industry. The additional thing needed is what was proposed several years ago for an independent steel company but was not made effective; that is a "staff" composed of a small group of men who have had much practical experience in the company along the lines of engineering, sales, operating, cost analysis and executive work. Such a staff of executives should have authority without routine responsibilities; they would study the problems of metallurgy, raw materials, new processes, new products and methods with the view of having their company prepared for the "financial dangers of sudden obsolescence."

Mr. Ramseyer's suggestion regarding oxygen is only part way good, because his plan still involves the handling of tremendous weights and volumes of inert material. It is expensive to pump, to heat, to convey and blow into a blast furnace three and three-tenths as much air by weight as the tonnage of iron produced. That is the chief reason that a blast-furnace plant requires so much capital investment. The CO_2 gas would be excess weight and volume just as the nitrogen is now; it would be a "revolving fund" of expense, similar to the excessive scrap that used to go round and round through the rolling mill and the open-hearth furnaces without adding anything to the tonnage of the steel plant. I think it would be better for us to begin our blast-furnace research work with a study of the hearth of the furnace and of the reactions that take place between the tuyere level and the level of the iron notch. This is the region that has not been sufficiently explored.

Mr. Ramseyer has not mentioned the fact that the blast furnace puts too much carbon into the pig iron, to be removed by the subsequent steps in making steel; and the bigger the furnace hearth, the more carbon goes into the pig iron. Even in foundry work lower carbons make better castings. A process of making iron with much lower carbon contents than our present pig iron is a subject worthy of research.

T. T. READ,* New York, N. Y. (written discussion).—Mr. Ramseyer suggests that arrangements might be made whereby the liquid phases of the contents of a blast furnace—slag, and pig iron—might be drained off continuously, thus turning it into what might be called a dry operation. He concludes that "the advantages of such a constant knowledge of the quality of the product would be manifold." Several years ago I considered this possibility for a different, and more weighty, reason. The blast furnace yields metal that contains, say, 70 or 80 lb. of carbon per ton. In the subsequent steel-making operation practically all this carbon is removed under conditions and with equipment which Mr. Ramseyer has characterized in somewhat satirical terms. The question, "Why let that carbon get into the pig iron when its removal is so laborious?" immediately suggests itself, and the next question is whether it is possible to prevent so much carbon getting into the fused metal. The general assumption seems to be that it is impossible, but it is at least doubtful whether such an assumption is valid. It is true that when almost carbon-free metallic iron was made in primitive furnaces by the so-called direct process, it yielded solid, unfused metal.

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But it does not follow that a modern furnace would have to produce unfused nearly carbon-free metal, for it certainly would not be impossible to attain the same temperature in the hearth of a modern blast furnace as that at which low-carbon steel remains liquid in an open hearth. S. P. Kinney's careful study of what goes on within a blast furnace does not indicate that in the lapse of time between the reduction of FeO to Fe and the fusing of the Fe the iron takes up all the carbon it contains when it issues from the tap-hole; it seems reasonable to assume that a considerable part of the carbon is taken up from the coke, which the superincumbent charge pushes down into the pool of fused metal that forms the lowest layer on the hearth, a contact that is maintained for a time expressed in hours rather than in minutes. If the liquid iron were drained away from the hearth as fast as it fuses it would, it seems reasonable to assume, come away much lower in carbon content than a typical pig iron. Whether it would also be lower in sulfur than a typical pig iron is not clear, but is at least possible; if it proved true, it would be an important additional advantage.

The higher temperature at which the lower-carbon metal would issue from the blast furnace would be an advantage in the subsequent steelmaking process. Is there, indeed, any fundamental reason why the thermally efficient blast furnace cannot produce a metal so hot that scrap would melt in it much as sugar melts in a cup of coffee? It does not require a vivid imagination to visualize the tap-hole of a blast furnace as leading directly to a point beneath the slag layer in an adjacent open hearth, into which both slag and metal would drain continuously. It would have to be maintained at a much higher temperature than the familiar settler into which a copper blast furnace continually discharges its fused products, but maintaining it at that temperature would not involve any practical problem that seems impossible, or even particularly difficult, of solution.

Since ability to secure patent protection on any developments along such lines would probably have considerable bearing on the willingness of a single corporation to spend money on experiment, I made a hasty survey of existing patents and found, to my surprise, that there are a number that apparently have some bearing on the matter. This, with the pressure of more immediate matters of concern, caused me to drop it, but it still seems that the possibility of useful developments along the lines suggested is large enough to justify the expense and time involved in following it up.

J. W. KINNEAR, JR.,* Munhall, Pa.—The author brings out one point that is absolutely in error; that is, that the modern blast furnace is as efficient as the modern open hearth. The figures have been worked out very carefully and net efficiency of the best open-hearth furnace today is higher than that of the best operated blast furnace today. Also in defense of the open hearth, I wish that we were in a position as open-hearth men to be able to sell steel at the same specifications at which the blast-furnace men are able to sell iron. It must be proved that the blast furnace or any shaft type of furnace can be controlled to within the modern steel specification limits. At present the blast furnace produces iron varying 0.5 per cent in silicon from cast to cast, while the open-hearth furnace is expected to meet a five point carbon specification on check analysis. And this reminds me—with full respect for old Captain Bill Jones, for he was a wonderful blast-furnace man in his time—of the first time a chemist came into the blast furnace where Captain Jones was working and started to analyze iron for sulfur, he said, "If they let that fellow loose, he is going to ruin the iron industry."

A. ZENTNER,† New York, N. Y.—A remark by a prominent nonferrous metallurgical engineer that if he could begin over again he would go into ferrous metallurgy,

* Assistant Open-hearth Superintendent, Carnegie Steel Co.

† Consulting Metallurgical Engineer.

because he felt that there were the large opportunities there for improving practice, caused me to become interested.

My remarks are made in a friendly spirit, not as sweeping criticisms. I would say that it is a surprise to note the extent to which batch processing is followed, and the extent to which heat is lost. Several of the practices seem rather rule-of-thumb for the scale of operations on which they are conducted.

Recently I had occasion to go into electrolytic iron for a client. Looking over the work that has previously been done, my observation was that the great bulk of it has been done by men who were thinking in terms of liters and gallons. If such a process is to be put over with a low-priced product, which it will have to be, the outlook, the viewpoint of the man developing it, must be in tons, tons of metal and tons of solution. It must be a comparatively large-scale operation and a few simple steps. The price of the product will not permit steps which—well, they must be more simple than with nonferrous metals.

Marcus Daly was one of the men back of the development of the Anaconda Copper Mining Co. One of his geologists was gone for a long time on a great many prospects, and he came back with a very long face. Daly asked him if he had found anything and he said, "No, not a thing." He was very pessimistic. Daly slapped him on the back and said, "Cheer up, man, go on out and spend some money." He meant, of course, don't be afraid to take an intelligent chance. That might help in taking an intelligent chance in some of the problems that confront us.

T. NAGEL,* New York, N. Y. (written discussion).—In excess of 3 billion cubic feet of 99.5 per cent purity oxygen was sold in the United States in 1929, the output from 156 plants which have production capacity to provide for the probable increase in demand for high-cost pure oxygen for many years to come. Largely supplied in cylinders and primarily used for welding and cutting metals, virtually 90 per cent of the pure oxygen sold in the United States was produced by the Linde and Claude interests. Practically all these oxygen plants are of small units, capacities under 5 tons oxygen daily output. Liquid-air plants are now being located adjacent to steel plants to supply gaseous oxygen through pipe lines on long-term contracts. The lowest price for this service, reported in 1932 was \$2.80 per 1000 cu. ft., equivalent to \$66 per net ton oxygen. High capital cost of plants and high production cost of pure oxygen have made the extensive use of oxygen prohibitive in metallurgical and other industries.

Availability of Oxygen.—The U. S. Bureau of Mines says (*Rept. of Investigations*, No. 2502, p. 4): "In view of the many recent developments in oxygen manufacture, and considering the increasing cost and decreasing quality of our raw materials, the Bureau of Mines, Department of the Interior, has taken the matter of the application of oxygen or oxygenated air to the metallurgical centers for consideration and has appointed an Advisory Committee to study the problem.

"This committee has made a thorough survey of the existing processes for the manufacture of 99 per cent oxygen. The conclusions reached by this survey are that the comparatively small demand for the product has prevented the installation of large units suitable for metallurgical processes, with corresponding economies, and by far the greater proportion of the present cost of oxygen represents the cost of transportation, storage and service. Large oxygen manufacturing plants can be built to serve metallurgical purposes directly, which, by virtue of their large production and correspondingly increased efficiency, together with the fact that no compression in cylinders, storage, transportation, or service will be required, will be capable of delivering oxygen for the processes at a cost not to exceed \$3 per gross ton. In

* Vice President and Chief Engineer, Carburetted Gas, Inc.

other words, the Committee finds that the oxygen industry is now able to make plants for supplying large quantities of oxygen to metallurgical industries at low cost."

Post-war improvements in the art of air liquefaction and rectification have made rapid strides in effecting a radical reduction of the initial air compression, and as power consumption is the major cost item of oxygen production the influence that reduced pressure makes in production cost of oxygen as well as lower cost of plant equipment is readily seen. Lower plant cost is further realized when producing gaseous oxygen of 95 per cent purity with recovery of 95 per cent of the oxygen content of the compressed air in contrast with the high oxygen loss entailed in rectifying oxygen to a purity of 99.5 per cent. Air-liquefaction plants producing 95 per cent purity oxygen at the site of consumption can provide gaseous oxygen at a plant production cost of \$3.50 per net ton with power at $\frac{1}{2}$ ¢ per kilowatt-hour, and \$5 per net ton with power at $\frac{3}{4}$ ¢ per kilowatt-hour when producing at the rate of 150 tons daily from three single units, capacity each of 50 tons. These oxygen costs are equivalent to 15¢ and 21¢ per 1000 cu. ft. respectively.

Of the many uses in the chemical and metallurgical industries for low-cost oxygen are numerous sluggish thermal operations which can be energized and improved by the use of crude oxygen to effect increased output of improved quality, effecting substantial cost reductions in operations. For example, a judicious use of oxygen enrichment of the open-hearth hot blast will raise the furnace temperature as much as 500° F., speeding up reactions to increase furnace output and lower production cost.

Oxygen for Pig-iron Blast-furnace Operation.—Fifty thousand cubic feet cold air blast enriched with 7400 cu. ft. 95 per cent oxygen will produce the same volume of hearth gas and the same hearth-gas temperature produced by 60,000 cu. ft. hot blast entering the tuyeres at 1250° F. The significance of this statement is that the cost of 150 kw-hr. required for producing oxygen enrichment of the cold blast per gross ton pig iron will eliminate the operating and maintenance cost of hot-blast stoves and provide greater control and flexibility of operation.

Investigations have demonstrated that slight enrichment of the hot blast will effect decided cost economy in pig-iron production by increasing the furnace output. A 1000-ton furnace would have its capacity increased to 1250 tons pig iron with no additional operating payroll, so that the net cost of the 250 tons increase in output would be the cost of its furnace burden.

For producing 95 per cent purity oxygen, air liquefaction and rectification plants design, plant-construction costs, plant-operation costs, technologists experienced on process and plant design, fabrication and operation also patent protection covering process and design, are available for providing low-cost oxygen plants producing low-cost crude gaseous oxygen at flexible capacity output to meet continuous operating requirements.

W. J. REAGAN,* Oakmont, Pa.—Mr. Ramseyer's vision of our future steel plant is highly interesting. However, I believe he has painted too black a picture of our present open-hearth methods. I believe that our open-hearth furnace and its method of operation have shown definite signs of progress during the past few years. Mr. Ramseyer says that our present open hearths operate at a thermal efficiency of only 10 to 15 per cent. McLoughlin, in his Thermal Study of an Open-hearth Furnace, presented before the American Iron and Steel Institute in 1931, shows that a well insulated furnace studied during this test operated at an efficiency of 27.8 per cent. I have no doubt that many of our present open-hearth furnaces are operating at a figure well over this one. Of course, these figures can be improved considerably.

* Edgewater Steel Co.

Also, there are open-hearth furnaces operating that have a charge weighing over 400 tons and producing about 500 tons every 24 hours.

In spite of the larger tonnages and greater operating efficiencies we still cannot greatly speed up the elimination of carbon, which is the principal chemical reaction in the open-hearth process. It is my belief that much research still remains to be done, possibly along the line pursued by Dr. Herty in conjunction with the Metallurgical Advisory Board, before we are able to make any radical changes in open-hearth practice.

It is impossible to discuss in detail most of the suggestions made by Mr. Ramseyer, for the simple reason that we know nothing about such a process. I am sure all steel producers would welcome such a method of making steel, as it would eliminate much of the uncertainty in the present methods. As mentioned before, we are still in the dark about many fundamental reactions in the making of steel and in the slag-metal reactions that occur during the process. When these reactions are thoroughly worked out we may have some hope of a continuous process similar to the blast furnace. The high-speed handling of many tons of molten steel at temperatures of about 2900° F. presents a highly practical problem that seemingly cannot be tackled by methods other than those in present use.

R. S. DEAN,* Washington, D. C. (written discussion†).—Mr. Ramseyer's paper emphasizes, in an interesting way, the very many technologic defects in the present steel process. The inference, however, that no attempts are being made to rectify these defects is quite incorrect. I think it would be safe to say that our staff in the Bureau of Mines has invented half a thousand schemes all more thoroughly considered than that offered by Mr. Ramseyer. We too have secretly longed for a "Giant" or at least a regiment of "Comsomals" to try out these ideas on a 2000-ton per day scale. I say secretly, because after all we like to call ourselves scientists, and it is certainly no part of the scientific method to try out one's waking dreams on a 50,000,000-dollar experiment.

What we are doing is to patiently work out some of the elements that must be included in any revolutionary steel process. Papers have been presented at this meeting representing several years of painstaking work on the magnetic concentration of iron ores—a step that Mr. Ramseyer seems to have overlooked. Methods have also been developed for the direct production of steel from these purified iron ores and the properties of the resulting product have been studied. These studies are not production-control work nor yet studies in special alloys, as Mr. Ramseyer seems to think. They are important elements in new steel processes. We have hesitated to draw mental pictures of the whole process because there are still so many unanswered questions, but since the fashion has been set by the author of the paper under discussion we may as well give a rough idea of what we have in mind. Consider, for example, the highly purified ore mixed with a purified coal and passed through a heated chamber until a temperature of 1450° is reached. The mass is then passed continuously through a squeezer and rolls, giving directly a wrought iron suitable for many purposes for which steel is now used. If steel is desired it is only necessary to introduce a melting step after the squeezer. I am sure that more than half the details—the easy half—have been worked out. "The rest of the problem would require merely time, money, and technical imagination."

We are giving some attention also to one of the essential elements in any process such as the one outlined by Mr. Ramseyer; namely, rapid reaction between slag and metal. Recently this has been given considerable attention in France by

* Metallurgical Division, U. S. Bureau of Mines.

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Perrin. The emulsification and de-emulsification of slag in steel are problems not likely to be solved from a swivel chair.

I am quite in agreement with the objective of the author but to reach it we do not need "Giants"—only a little patience and support for the experimental metallurgists now on the job.

W. D. PUGH,* Sheffield, England (written discussion).—The steel industry is on the defensive, and no amount of excusing or explaining will affect the validity of Mr. Ramseyer's trenchant and timely criticism. Facts are difficult things to argue with, and Mr. Ramseyer's central fact—that the steel industry has made no fundamental progress in the last decade—cannot be challenged, except perhaps by Aston in America and Perrin in France.

The author speaks as a chemical engineer and "an outsider," but it is clear that he has had, and perhaps still has, close associations with this wayward industry. Critical as he is, he retains his sympathy for those engaged in their everyday work around blast furnaces and in steel mills; were it otherwise he would never have written this paper.

It would have been easy to log the shortcomings of the steel industry, but the author has bravely indicated lines along which process development can, and undoubtedly will, take place, and he has earned the praise, and thanks, of those within the industry who have been too long content to carry on in the way of their fathers and forefathers.

That Mr. Ramseyer's ideas will be condemned by many is certain; that he anticipates such condemnation is evident from his reference to Dr. Little's remarks on the History of Technical Development. In this connection Dr. Friedrich Bergius' comment, too, is of interest, coming from one who knows of the difficulties with which the inventor in large-scale industries has to contend:

"The counterforces of the outside world do not begin to make themselves felt as long as an invention remains far removed from its final state of development . . . It is very seldom that an invention of any note does not meet with some resistance from those in control of already established industries . . . In the later development stages ample financial means are necessary."

The next move lies with those responsible for the conduct of the steel industry. There is, among those engaged in industry, the necessary imagination and technical ability, and if the money necessary for development work is made available, there is no reason why the somewhat revolutionary changes indicated by Mr. Ramseyer should not soon become actualities.

As a means to this end, why not a Cooperative Process Research Committee for the Iron and Steel Industry, preferably international in character? In England we have always associated the United States with "that energy, enthusiasm and lack of respect for precedent" with which Mr. Ramseyer credits Russia. Will the New Deal in industry go hand in hand with a New Deal for research in the steel industry? We await with absorbing interest the next step of those who control its destinies.

C. F. RAMSEYER (written discussion).—I agree with Mr. Sweetser that the mere creation of a research department is not all that is necessary for progress in industry; an adventurous and imaginative research committee composed of the executive heads of the business is also a vital necessity.

Professor Read mentions the bearing of patent protection on the willingness of a single corporation to spend money on experimental work. It has, of course, an even greater bearing on the willingness of a number of competitive companies to support

* English Steel Corporation, Ltd.

cooperative work, especially when that work is likely to be very expensive, since there is a great danger that any savings made will tend to be passed on to the consumer through competition without any one of the companies concerned getting a definite individual return on its research investment.

I was glad to learn of Mr. Nagel's figures on the present-day cost of oxygen. I feel, however, that instead of 50-ton per day units and \$3.50 per ton costs, oxygen will have to be available in 500-ton units and at costs around a dollar a ton, really to interest the steel industry. His figures are for 95 per cent oxygen. In making special quality nitrogen-free steels equal to those made from wrought or sponge iron, it might not be desirable to leave even 5 per cent nitrogen in the oxygen supply.

The Bureau of Mines has done and is doing extremely valuable work both in fundamental research and on new process possibilities. I did not intend to include the Bureau as a part of the "backward steel industry." I must differ with Mr. Dean, however, on several points. I feel that enough fundamental work has already been done on slag-metal reactions to enable process development work to go forward without waiting for further data, useful as these might be. Magnetic concentration violates the chemical engineering principle of working in the liquid phase whenever possible, a principle based on the greater speed of reaction obtainable, the greater ease of handling and the easier applicability of countercurrent methods. In iron and steel it also means higher temperatures with consequent additional increase in reaction rates. Low capacity per unit of investment cost, with its resultant high labor cost, I believe is the main factor against the so-called direct reduction processes, workable as they may be on a small scale. On the other hand, in the liquid phase the efficiency of continuous processes frequently tends to increase as the units grow larger. Four men per shift operate the latest 20,000-bbl. per day oil stills. 20,000 bbls. of liquid steel per day would run over 7,000,000 tons in a 300-day year! or more than any single steel plant in the world can produce—yet it is only equivalent to two continuous 3-in. diameter nozzle streams under a head of some six feet.

Mr. Dean concludes with a plea for "patience and support for the experimental metallurgists now on the job." At the rate the industry has progressed in the past, patience will surely be required.

Solubility of Nitrogen in Liquid Iron*

BY JOHN CHIPMAN,† MEMBER A.I.M.E., AND DONALD W. MURPHY†

(New York Meeting, February, 1935)

RECENT developments in iron alloys containing nitrogen have indicated that this element may exert a considerable influence on the properties of the metal. This influence is not always in an undesirable direction and the indications are that nitrogen should be regarded as an alloying element, the amount of which should be subject to control, rather than as an inherently deleterious impurity. In controlling this element in liquid iron to the best advantage, it is necessary to have a reliable background of fundamental data pertaining to solubilities, rates of solution and chemical reactions of nitrogen in liquid iron. Obviously, the first step in such an investigation is the determination of the solubility of nitrogen in pure iron, and this has been the object of the experiments described in this paper.

The solubility of nitrogen in solid iron has been measured by Jurich,¹ Sieverts,² Martin,³ and Iwasé⁴ and the agreement among the first three inspires confidence in their results. No accurate determinations of its solubility in liquid iron have been recorded though several investigators have obtained approximate results. Strauss⁵ was able to introduce 0.03 to 0.04 per cent nitrogen into steel by the action of either ammonia or nitrogen on the liquid metal. This was accomplished by Eilender and

* This paper presents the results of one phase of an investigation of nitrogen in steel which was undertaken in cooperation with The Timken Steel and Tube Company. Manuscript received at the office of the Institute Oct. 16, 1934.

† Department of Engineering Research, University of Michigan, Ann Arbor, Mich.

¹ E. Jurich: Dissertation, Leipsig, 1912. (Quoted by Sieverts.)

² A. Sieverts: *Ztsch. f. Metallkunde* (1929) **21**, 37. *Ztsch. f. physik. Chem.* (1931) **155**, 299.

³ E. Martin: *Archiv. f. Eisenhüttenwesen*, (1929) **3**, 407. *Metals & Alloys* (1930) **1**, 831.

⁴ K. Iwasé: *Sci. Repts.* Tohoku Univ. (1926) **15**, No. 4.

⁵ B. Strauss: *Stahl u. Eisen* (1914) **34**, 1814.

Wasmuht⁶ also. Andrew⁷ melted iron under nitrogen at 200 atmospheres pressure and obtained a product containing 0.30 per cent nitrogen. Sawyer⁸ used a range of pressures up to three atmospheres and found that his results and Andrew's could be expressed by the formula:

$$\text{Per cent nitrogen} = 0.02\sqrt{P}$$

where P is the pressure in atmospheres. None of these investigators have shown that actual saturation of the iron was attained. In Sawyer's experiments an undetermined amount of nitrogen was evolved from the metal during solidification and his analytical results are therefore certainly lower than the true solubility.

PLAN OF INVESTIGATION

The method used in this investigation consisted in melting a charge of iron in a closed induction furnace under an atmosphere of nitrogen, holding the melt at constant temperature until absorption was complete, then cooling and analyzing the resulting ingot. The induction method of heating was used for the reasons that: (1) it permitted the use of fused silica furnace tubes which are quite gastight below 1000° C.; (2) the stirring action of induction heating was advantageous in decreasing the time necessary to complete the absorption, and (3) fairly accurate temperature control was possible.

The absorption of nitrogen was followed by making such successive, small, measured additions of nitrogen from a burette as were required to maintain the pressure in the system at atmospheric. Each heat was therefore continued until no changes in burette reading occurred over a period of time. It might be pointed out here that equilibrium was approached in one direction only. The criterion that equilibrium had been established depended upon the fact that, as the solution approached saturation, the rate of absorption approached zero. This condition, therefore, was attained by prolonging the heats until no volume changes in the system, as indicated by burette readings, occurred over a considerable period of time.

The melts were allowed to cool under an atmosphere of nitrogen and the resulting ingots sectioned lengthwise into quarters or halves for analysis. The direct analysis of ingots was chosen to determine solubility, rather than calculations based upon the amount of nitrogen admitted, for several reasons. First, the amount and tightness of packing of the alumina about the alundum thimble was difficult to standardize and would, of course, cause different amounts of nitrogen to be used. Second,

⁶ W. Eilender and R. Wasmuht: *Metals & Alloys* (1930) **1**, 732.

⁷ J. H. Andrew: *Iron and Steel Inst. Carnegie Schol. Mem.* (1911) **3**, 236.

⁸ C. B. Sawyer: *Trans. A.I.M.E.* (1923) **69**, 798.

in spite of precautions, bridging of the heat occurred, frequently producing very wide variations in the weight of ingots and leaving an indeterminate amount of solid metal. Third, the temperature distribution in the furnace under various conditions that would influence any calculation was a totally unknown factor. Fourth, much of the absorption of gas was accomplished before even approximately steady states of temperature distribution had been attained, which would considerably increase the errors in calculation.

Many other conditions might conceivably complicate a method based upon the amount of nitrogen admitted while the direct analysis had perhaps only one major source of error; namely, segregation. In preliminary experiments nitrogen was bubbled through molten iron until saturation was believed to have been attained, after which the entire charge of iron was cast into an ingot mold and allowed to solidify. Not only was it difficult to reproduce results because of the absence of any definite criteria of saturation but also the segregation of nitrogen and other impurities was quite marked. However, by decreasing the size of the melts to about 100 grams, it was possible to eliminate difficulties due to segregation. The small size of the charge used in the later heats permitted the use of an entire quarter or half of the ingot in analysis, which made it possible to secure more representative samples.

ANALYSIS OF INGOTS

The determination of nitrogen in the saturated iron-nitrogen ingots was made by the vacuum fusion method in an apparatus similar to that described by Vacher and Jordan,⁹ with some modifications to promote greater accuracy. In this method the steel is melted in a graphite crucible under high vacuum and the gases resulting from the fusion, consisting chiefly of hydrogen, carbon monoxide and nitrogen, are stored under low pressure until the treatment of the metal is complete.

The graphite crucible was exhausted at 1600° C. to a pressure of about 0.001 mm. of mercury, the sample of steel or iron introduced and evacuation continued until the pressure had again fallen to approximately 0.001 mm. when the treatment was considered complete. The evacuation of the steel usually required about 15 min. except when zirconium was present, in which case the time was somewhat longer although the evolution of gas was fully as complete. The gases so obtained were analyzed by circulation over copper oxide at 300° C., and subsequent absorption of the resultant water vapor and carbon dioxide in phosphorus pentoxide and ascarite. The residual gas, after elimination of water vapor and carbon dioxide, is considered, on the basis of previous

⁹ H. C. Vacher and L. Jordan: U.S. Bur. Stds. *Jnl. of Research* (1931) **7**, 375.

work by other investigators, to be nitrogen. The decrease in pressure accompanying each absorption is, of course, a measure of the quantity of gas absorbed and may readily be converted to terms of weight per cent of the original metal sample.

The volume calibration of the vacuum fusion apparatus was carried out with pure nitrogen admitted from a carefully calibrated burette. In the calculation of gas content it was necessary to apply blank corrections for the gases evolved from the crucible itself. For the average 15-min. period these amounted to 0.000008 gram of hydrogen, 0.00005 gram of oxygen and 0.00004 gram of nitrogen. Expressed in terms of weight per cent based on a 20-gram sample, these were 0.000004 per cent hydrogen, 0.00025 per cent oxygen and 0.0002 per cent nitrogen. The systematic errors in analyses amount to about 0.0005 per cent while accidental errors arising from segregation and other sources in this case amount to an additional 0.0005 per cent. The analyses are therefore accurate to about one in the third place.

EXPERIMENTAL METHOD

The apparatus as finally developed for this study is shown in Fig. 1. The charge was placed in an alundum thimble *Q* and the thimble was then packed in crystalline alumina *I*, in the silica furnace tube *H*. The furnace tube was about 40 mm. inside diameter and 18 cm. long. The molybdenum wire coil *P* was placed over the charge, and the fused silica tubes *D* and the porcelain sight tube *E* used to decrease the amount of gas space in the furnace tube were placed in position before the pyrex glass cap *C* was sealed in place. The molybdenum wire coil was used in an effort to eliminate bridging, always a serious difficulty in induction melting. The coil was heated by induction to approximately the temperature of the liquid metal. Although this expedient was only partially successful in preventing complete bridging, it was always possible to melt down enough of the bridge to obtain temperature readings. The elbow tube *K*, containing silicon-zirconium alloy, was placed in position and evacuation begun.

During the preliminary evacuation the furnace assembly was repeatedly flushed by admitting purified nitrogen from the burette *B*. After the preliminary evacuation, a small electric furnace was placed around the furnace tube just below the water-cooling coils *G*. The bake-out was carried on for about 2 hr. at a temperature of 920° to 970° C., during which time the pressure in the entire system was kept below 0.002 mm. of mercury.

Upon completion of the bake-out, the furnace was removed and the induction coil *O* was substituted. The charge was then heated by induction to a temperature just below the melting point of iron and

evacuation stopped. Successive measured additions of nitrogen were then made until atmospheric pressure was attained, after which the charge was melted and raised to the desired temperature.

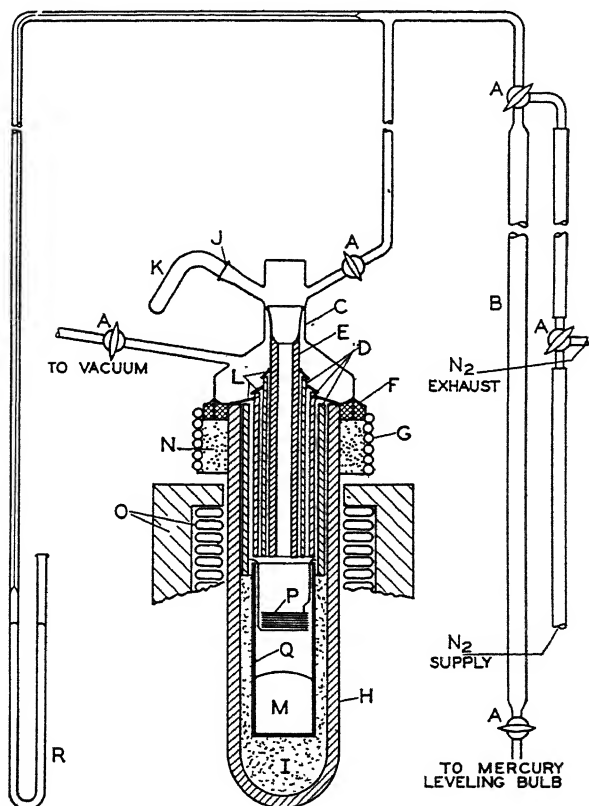


FIG. 1.—APPARATUS.

- | | | |
|-------------------------------|-----------------------------|--------------------------|
| A. Stopcocks. | H. Fused silica furnace | tubes. |
| B. Burette. | tube. | M. Melt. |
| C. Pyrex glass cap. | I. Crystalline alumina | N. Zinc cement. |
| D. Fused silica filler tubes. | packing. | O. Induction coil. |
| E. Porcelain sight tube. | J. Ground glass joint. | P. Molybdenum wire coil. |
| F. Piccin seal. | K. Elbow alloy tube. | Q. Alumundum thimble. |
| G. Water cooling coils. | L. Coil supports for filler | R. Mercury manometer |

During the run frequent temperature readings were obtained with the optical pyrometer. The pyrometer was sighted through a reflecting prism and the flat portion of the glass cap down the porcelain sight tube to the metal surface. Under these conditions, the true temperature of the metal is not observed, but rather, a temperature comparable to that which would be obtained by sighting on steel in the open. Consequently

the Bureau of Standards¹⁰ corrections for observed temperatures of steel in the open were applied. During the initial period of heats 19, 20 and 21 the temperature was adjusted so that both liquid and solid iron could be observed in the bath. The observed temperature, corrected as described above, indicated a melting point of about 1520° C. This was considered a sufficiently good check on the accepted melting point, 1530° C., to warrant the use of this system of temperature corrections over the entire range. The probable error in measurement at the lower temperatures was about $\pm 10^\circ$ C., while at the upper temperatures the error was probably $\pm 30^\circ$ C.

The pressure in the furnace was maintained at atmospheric level by repeated measured additions of nitrogen from the burette. The run was continued at approximately constant temperature until the burette reading had been constant for from 15 to 40 min. In certain heats 0.7 gram of silicon-zirconium alloy was added just before the power was turned off by rotating the elbow tube *K* through 180°.

The charge used in heats 12 to 17, inclusive, consisted of about 100 grams of electrolytic iron previously melted in vacuum. The charge in the remaining heats was about 85 to 100 grams of electrolytic iron disks not previously treated except for the usual cleaning in alcoholic hydrochloric acid. These irons had the following analyses:

| | C | Mn | Si | S | P | O | N |
|------------------------------|-------|-------|-------|-------|-------|--------|--------|
| Electrolytic-iron disks..... | 0.027 | 0.008 | 0.001 | 0.007 | 0.002 | 0.0138 | 0.0002 |
| Vacuum melted..... | 0.013 | | | | | 0.0119 | 0.0000 |

In certain heats, in addition to these materials small amounts of high-aluminum or high-silicon irons, previously melted in vacuum, were added to the charge. These were introduced with the original charge in a position near the bottom of the thimble to insure complete melting of the alloy iron.

The crucibles used were alundum extraction thimbles, grade R.A.84, supplied by Norton Company. The thimbles were about 27 mm. inside diameter by 80 mm. in length. These were found to give excellent service even at the highest temperatures, although from the nature of the apparatus it was necessary to use a fresh crucible with each heat.

The nitrogen supply was commercial water-pumped nitrogen, for which the manufacturer claimed a purity of 99.75 per cent. This was purified by passing through ascarite, phosphorus pentoxide and a silica tube containing metallic copper at about 500° C.

¹⁰ G. K. Burgess: U.S. Bur. Std. *Tech. Paper* 91 (1917).

CORRECTION FOR EVOLUTION ON SOLIDIFICATION

As soon as the power was cut off the entire furnace began to cool rapidly, resulting in a contraction of the gas contained in the dead space of the furnace. When gas was evolved from or absorbed by the ingot during cooling, an additional volume change was superimposed upon the normal contraction. Burette readings were taken at 30-sec. intervals during the cooling of each heat, the pressure being always maintained at atmospheric. Typical curves in which the burette readings are plotted

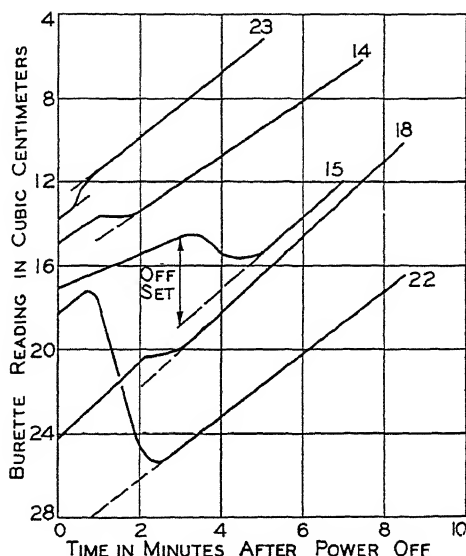


FIG. 2.—METHOD OF DETERMINING EVOLUTION OF GAS ON COOLING.

against time are shown in Fig. 2. The curves for heats 14 and 18 show the normal contraction on cooling with a slight offset due to the halt in cooling at the temperature of solidification. Heats 13, 14, 17, 18, 19 and 20 behaved in this manner, and the average offset was found to be 1.4 c.c. The ingots were sound and there was no reason to suspect that gas was either absorbed or evolved during solidification. In other cases considerable gas was evolved, resulting in a porous or hollow ingot. The offsets in curves 15 and 22 amounted to 4.2 and 10.9 c.c., respectively, which, allowing for the normal offset of 1.4 c.c., corresponds to the evolution of 2.8 and 9.5 c.c. of gas. These amounts were calculated to a weight basis and are given in column 7 of Table 1 as corrections to the percentage of nitrogen in the ingot. In other cases, illustrated by curve 23, an absorption of nitrogen occurred. This absorption usually resulted from the addition of silicon-zirconium and in all such cases the surface of the ingot was covered with yellow particles of zirconium nitride. Since the

surface was always removed before analyzing the ingot, we have not considered it necessary to apply a correction for absorption.

TABLE 1.—*Experimental Data on Solubility of Nitrogen in Liquid Iron*

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|-------------------|-----------------------------|-----------------------|---------------------------------|--------------------|--------|--|--|--------------------------|
| Heat No. | Temper- ature Deg. C. | Condition of Ingot | Weight of Ingot, Grams | Analysis, Per Cent | | Evol- ution on Cooling, Per Cent | Nitro- gen in Melt, Per Cent | Rate Coeffi- cient |
| | | | | O | N | | | |
| | | | | | | | | |
| 10 ^{a,b} | | Hollow | 79 | 0.003 | 0.0277 | ? | | |
| 11 ^c | 1600 | Hollow | 65 | 0.002 | 0.0303 | 0.0103 | 0.0406 | 28 |
| 12 ^c | 1610 | Slightly porous | 101 | 0.026 | 0.0410 | | 0.0410 | 2.6 |
| 13 ^c | 1600 | Slightly porous | 88 | 0.023 | 0.0396 | 0 | 0.0396 | 2.6 |
| 14 | 1600 | Sound | 49 | 0.017 | 0.0421 | 0 | 0.0421 | 3.2 |
| 15 | 1680 | Sound | 61 | 0.005 | 0.0344 | 0.0050 | 0.0395 | 2.6 |
| 16 ^{a,b} | 1670 | Sound | 77 | 0.034 | 0.0440 | | | 2.8 |
| 17 | 1760 | Sound | 72 | 0.010 | 0.0426 | 0 | 0.0426 | 2.3 |
| 18 | 1760 | Sound | 84 | 0.032 | 0.0424 | 0 | 0.0424 | |
| 19 ^b | 1540 | Sound | 74 | | | 0 | | 3.5 |
| 20 | 1540 | Sound | 62 | 0.020 | 0.0390 | 0 | 0.0390 | 1.7 |
| 21 | 1540 | Porous | 70 | 0.017 | 0.0376 | 0.0017 | 0.0393 | |
| 22 ^d | 1610 | Hollow | 75 | 0.006 | 0.0276 | 0.0139 | 0.0415 | 55. |
| 23 ^{a,d} | 1650 | Piped | 85 | 0.007 | 0.0375 | | 0.0375 | |

^a Heats 10 and 11 contained respectively 0.07 and 0.15 per cent aluminum.

^b Heats 10, 16, 19 not plotted in Fig. 3.

^c 0.70 gram silicon-zirconium (Zr 36 per cent) was added to heats 12 and 23, fifteen seconds before power was turned off, to heat 16 three minutes before, and to heat 13 five seconds after power was turned off.

^d Heats 22 and 23 contained 0.70 per cent silicon in charge.

SOLUBILITY OF NITROGEN IN LIQUID IRON

A summary of all experimental results is given in Table 1. Columns 3 and 4 give the weight and condition of the ingot; 5 and 6 the gas content as determined by vacuum fusion analysis. Column 7 shows the correction for evolution of gas during cooling, and Column 8 contains the corrected nitrogen content of the melt. When no alloy addition was made and no gas was evolved on cooling, the data of column 8 are believed to be reliable within one unit in the third place of decimals. When large volumes of nitrogen were evolved on solidification, notably heats 11 and 22, the uncertainty is considerably greater. The addition of the zirconium alloy just before the power is turned off is believed to have seriously affected the result in only one heat; in heat 16, when the alloy was added 3 min. before the power was turned off. This ingot contained a higher percentage of nitrogen than any other, and, since we have

no data on the amount absorbed after the alloy addition, this heat is omitted from consideration.

The solubility of nitrogen is plotted as a function of temperature in Fig. 3. The barometric pressure throughout this series of determinations ranged from 735 to 743 mm. It has not been considered necessary to

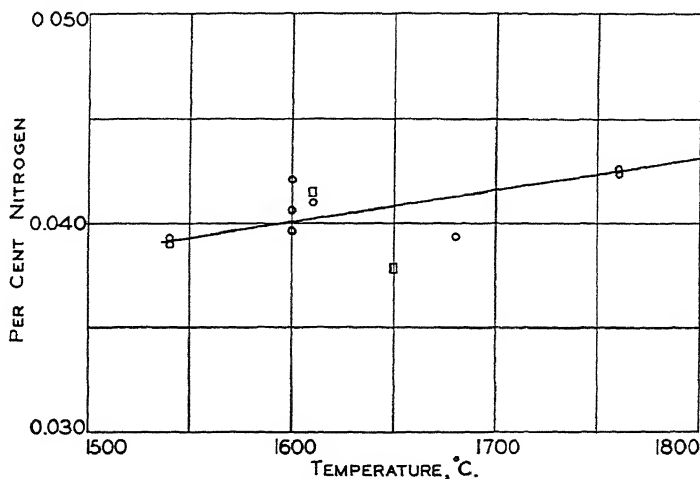


FIG. 3.—SOLUBILITY OF NITROGEN IN LIQUID IRON.

take account of these fluctuations in recording the results, since the experimental errors are larger than any possible effect of these small variations in pressure upon the solubility. The data may be considered therefore as representing the solubility of nitrogen at a pressure of 740 mm. It is evident that the temperature coefficient of solubility is small, of the order of 1.5×10^{-5} per cent per degree.

It has been suggested repeatedly that the presence of nitrogen in steel is due to the absorbing power of impurities rather than to the solubility of nitrogen in liquid iron itself. Since the melts were made in alundum thimbles, the possibility of contamination of the metal by aluminum or silicon must not be overlooked. The ingots from four typical heats were analyzed for silicon, with the following results:

| | | | | |
|------------------------|-------|-------|-------|-------|
| Heat No..... | 11 | 14 | 17 | 18 |
| Per cent, silicon..... | 0.021 | 0.020 | 0.044 | 0.023 |

It is conceivable that these small amounts of an active impurity might affect the solubility of nitrogen. If the solubility is affected by such small percentages, it should be influenced to a much larger extent by a higher percentage, therefore heats 22 and 23 were made, each containing approximately 0.70 per cent silicon. The nitrogen contents of these two heats are shown as squares in Fig. 3. Within the probable errors of the experiments these two heats are in agreement with those in which

no silicon was added. The only conclusion that can be justified on the basis of these data is that silicon does not appreciably affect the solubility of nitrogen in liquid iron.

Heats 10 and 11 contained, respectively, 0.07 and 0.15 per cent aluminum in the charge. The data on heat 10 are incomplete because of failure to observe the evolution of gas on cooling. Heat 11, however, is quite in line with the other heats, and it is impossible to escape the conclusion that small amounts of aluminum have no great effect upon the solubility of nitrogen.

RATE OF SOLUTION OF NITROGEN IN IRON

Although a study of the speed with which nitrogen dissolves in liquid iron was not the primary purpose of this investigation, the data on most

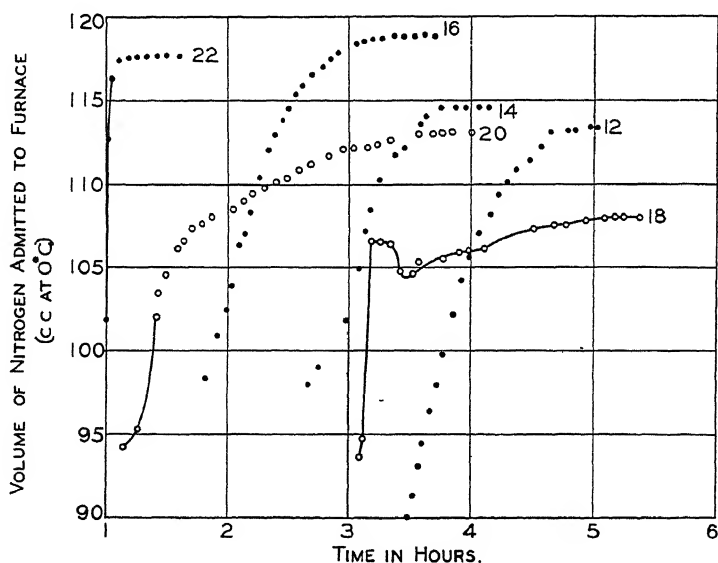


FIG. 4.—EXPERIMENTAL DATA ON RATE OF SOLUTION.

of the runs are sufficiently complete to serve as the basis for some interesting conclusions regarding the factors that may affect the rate of solution. The data on six experiments are shown in Fig. 4, in which the volume of gas admitted to the furnace, reduced to 0° C., is plotted against time. The rate is somewhat irregular during the first few minutes of each run, owing to the adjustments in power that had to be made in order to bring the charge to the desired temperature. In all cases the approach to saturation is uniform.

The simplest mathematical expression for the rate of solution of a gas in a liquid, where the temperature and pressure of the gas remain constant, is

$$\frac{dx}{dt} = k(n - x)$$

where x is the amount dissolved at time t , n is the total amount dissolved at saturation and k is the rate coefficient. The value of k obviously depends upon numerous details of the experimental procedure such as the mass of the melt, the rate of stirring, and the nature and area of the gas-metal interface. These factors were at least comparable, though not exactly reproducible, in our experiments. The values of k for the various runs may therefore be used to show in a general way the effects of certain other factors upon the rate of solution. It should be emphasized that these values are of interest only in drawing comparisons and that k is in no sense a property of the iron-nitrogen system. In the absence of induction stirring, we should expect to find k values of a much lower order of magnitude. The above equation may be written

$$\frac{-2.3d \log (n - x)}{dt} = k$$

from which it is evident that when the logarithm of $(n - x)$ is plotted against time a straight line should be obtained with a slope of $-k/2.3$.

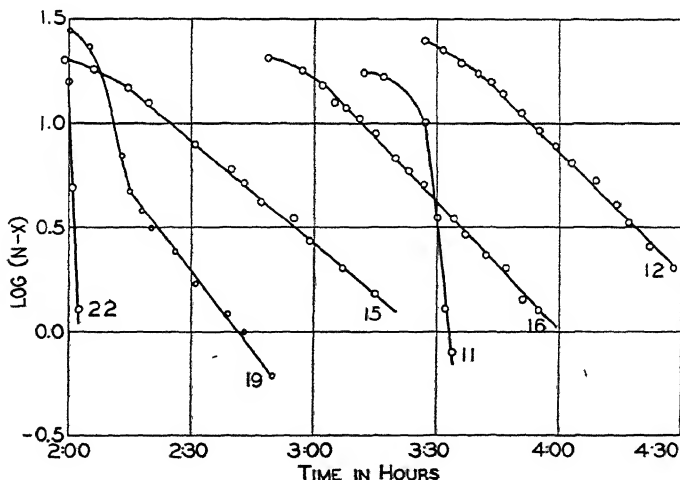


FIG. 5.—LOGARITHMIC PLOT OF RATE OF SOLUTION.

The data on several heats are plotted in this manner in Fig. 5, the values of $n - x$ being expressed in cubic centimeters of nitrogen at 0°C . Rate coefficients, in which t is expressed in hours, are given in column 9 of Table 1.

Comparison of these rate coefficients leads to two interesting conclusions, which must be regarded as tentative and subject to future experi-

mental verification, but which ultimately may be of the greatest importance in the control of nitrogen in steel manufacture. These tentative conclusions are:

1. The rate of solution of nitrogen in liquid iron is not appreciably affected by temperature, within the range of the present experiments.

2. The rate of solution is greatly affected by the presence of other elements, and small amounts of aluminum and silicon greatly increase the rate.

SUMMARY AND CONCLUSIONS

A simple method for determining the solubility of nitrogen in liquid iron has been devised. The solubility, at approximately 740 mm. pressure, was found to be 0.039 per cent just above the melting point and 0.042 per cent at 1760° C. (3200° F.).

Within the limits of experimental error, the solubility is not affected by 0.15 per cent aluminum or by 0.70 per cent silicon.

The rate of solution of nitrogen in liquid iron is not greatly affected by temperature. The presence of aluminum or silicon in the melt exerts a very great influence upon the rate of solution, the rate coefficient being increased tenfold to twentyfold in two experiments in which these elements were present.

DISCUSSION

(Eric R. Jette presiding)

H. C. VACHER,* Washington, D.C. (written discussion).—The authors have done very creditable work. The difficulties encountered in determining gas-liquid iron equilibria can be fully appreciated only by one who has attempted to make such determinations.

Determinations of aluminum and carbon and of silicon and carbon in ingots 11 and 22 respectively would be interesting. These ingots evolved gas during solidification and presumably contained enough aluminum and silicon to prevent evolution of carbon monoxide. Results obtained from ingots 14, 17, 18 and 20 indicate that liquid iron, which contains an appreciable amount of nitrogen, does not evolve gas during solidification. This in turn indicates that the dissociation pressure of iron nitride is approximately atmospheric pressure or less. The dissociation pressures of silicon and aluminum nitrides are known to be less than atmospheric pressure. Therefore the gas evolved from ingots 11 and 22 is not likely to be nitrogen if significant amounts of aluminum and silicon were present in the charge immediately before solidification. However, it is reasonable to believe that significant amounts of aluminum and silicon were present in the final ingots. Consequently the conclusions would be that carbon monoxide and not nitrogen was evolved from ingots 11 and 22, and, finally, that the presence of an appreciable amount of nitrogen in liquid steel diminishes the deoxidation action of aluminum and silicon.

J. B. AUSTIN,† Kearny, N. J. (written discussion).—In connection with the interesting conclusions drawn by the authors as to the influence of aluminum and

* Assistant Metallurgist, U.S. Bureau of Standards.

† Research Laboratory, U.S. Steel Corporation.

silicon on the rate of solution of nitrogen in liquid iron, I note in Table 1 that the ingots containing silicon and aluminum were also the ones that gave off the most nitrogen on cooling. I should like to ask the authors if they believe this would be generally true. For if it is, it suggests two possibilities: (1) That the presence of these alloying elements alters the inherent rate of dissolution as well as that of solution; or (2) that, since these ingots are highly deoxidized, the presence of fine particles of oxide may provide nuclei for the formation of bubbles of gas and so hasten the dissolution. In either case it would appear that the control of aluminum and silicon in the melt might in practice prove a convenient way of controlling the amount of nitrogen left in the iron after solidification.

I should also like to compliment the authors upon the care they have used in explaining the assumptions and the limitations involved in their work and in differentiating between the results they have established on a firm basis and those that should be accepted tentatively awaiting confirmation. It is not often that we find such a combination of good experimental work and clear presentation.

V. H. GOTTSCHALK,* Pittsburgh, Pa. (written discussion).—This new accurate value for the solubility of nitrogen in liquid iron was obtained by a method whose success depends on the failure of the gas to be evolved during cooling and solidification. Sawyer states that his solutions of nitrogen in liquid iron “spit” on solidification, and this is what might be expected when it is realized that, calculated to volumes, the 0.04 per cent of nitrogen dissolved at 1600° C. corresponds to 220 c.c. of gas in 14.5 c.c. of liquid metal and that only about half of this gas can be held in solution normally below the melting point. Computed to 0° and 760, this 220 c.c. would be only 32.0 c.c., but even in this milder form molten iron is revealed as a better solvent for nitrogen gas, volume for volume, than the twenty-odd liquids for which nitrogen solubilities are listed in volume III of the International Critical Tables. The values there given vary from 15.5 to 258.0 c.c. of nitrogen at ordinary temperatures dissolved in 1000 c.c. of solvent, while the 32.0 c.c. of nitrogen in 14.5 c.c. of liquid iron would correspond to 2200 c.c. in 1000 c.c. of iron.

Furthermore, the solubility of nitrogen in these ordinary liquids decreases with rising temperature and increases directly with the pressure, while the solubility in liquid iron is shown in Fig. 3 to increase with temperature and, as pointed out by Sawyer, increases with the square root of the pressure. This has all been discussed in a previous paper¹¹ emphasizing the fact that we understand very little of what we know about the solubility of gases in metals.

The system iron-nitrogen is complicated further by the contradictions concerning compound formation leading to nitrides of iron, which A. A. Noyes¹² has shown have dissociation pressures of many thousands of atmospheres—an observation checked recently by careful work at the Fixed Nitrogen Research Laboratory. In other words, not only are Fe_2N and Fe_4N so unstable that their existence in the solid state can be explained only in vague terms, but such compounds could not be formed at all by the action of molecular nitrogen on iron under any conditions. Sieverts' \sqrt{P} law may help here by indicating a preliminary dissociation of N_2 into active nitrogen atoms.

S. L. HORT,† Milwaukee, Wis.—Mr. Scheil and I expect to hand in a written discussion of this paper, so I will make only a few comments now. The authors have

* U.S. Bureau of Mines.

¹¹ V. H. Gottschalk and R. S. Dean: Solubility of Gases in Metals. *Trans. A.I.M.E.* (1933) **104**, 133.

¹² A. A. Noyes and L. B. Smith: The Dissociation Pressures of Iron Nitrides. *Jul. Amer. Chem. Soc.*, (1921) **43**, 475-481.

† Research Metallurgist, A. O. Smith Corporation.

done a splendid piece of work which will be appreciated by all who have worked in this field. I refer particularly to the requirements for getting experimental data on which can be based sound conclusions.

The point that Mr. Scheil and I discuss relates particularly to the forms in which nitrogen may occur in steel. I regard it as somewhat unfortunate that at this period more people are not engaged in determining fractional oxygens of iron and steel. Undoubtedly there is much information to be gained by that procedure. For instance, the authors show strikingly that silicon and aluminum both have some very definite effect on the behavior of nitrogen relative to iron. If the authors had analyzed their samples afterwards for fractional oxygen, I do not doubt that the nitrogen that occurred in those various samples would come off in different fractions.

At first sight that sounds like more or less of a grab in the dark, because why should you get nitrogen fractions at the same temperatures at which you get oxygen fractions? And yet that appears to be so. While we have not arrived at a position where we can make much use of the results, there do appear to be such things as fractional nitrogens just as there are fractional oxygens, and I believe some day those results will be definitely tied up with the behavior of the steel.

It is interesting, in this connection, that some of the recent work on additions made to mild steel for purposes of preventing aging effects, and so forth, relates to elements which loom up rather large in the nitrogen picture, like aluminum and titanium. They are, of course, deoxidizers, but at the same time we should not lose sight of the fact that they also have their own peculiar relationships with nitrogen.

J. CHIPMAN.—I think that Mr. Vacher's hypothesis that the evolution from the ingots treated with silicon is CO rather than nitrogen is most certainly erroneous, because I have never been able to observe the evolution of gas, from ingots containing silicon or aluminum, unless some such gas as nitrogen or hydrogen were present to a rather large extent.

The dissociation pressure of various nitrides has been studied. The dissociation pressure of silicon nitride at these temperatures is several atmospheres. In the presence of iron, which dilutes the silicon, it might be much greater. On the other hand, the dissociation pressure of aluminum nitride is supposed to be small, according to extrapolations of available data, and we were surprised to find on many occasions that it is not an effective dentrifier.

Dr. Austin's comments regarding the evolution of nitrogen and the possible explanations had occurred to us and we were on the verge of explaining the thing as being some sort of catalytic effect, which is just a statement to cover up our ignorance—we do not know how aluminum and silicon act to speed up the absorption of nitrogen, but it is quite possible that the mechanism by which the absorption of nitrogen is speeded up is very much the same as that by which the evolution of nitrogen is speeded up.

I think that Mr. Gottschalk is rather skeptical in this business. So was I in planning the work and before the results were obtained. I had never expected that an ingot saturated up with nitrogen, all that it could absorb from the gas, would be capable of solidifying without evolving nitrogen, because I know from sad experience that larger ingots do evolve nitrogen on solidification, evolve plenty of it, and bleed all over the place if there is enough of it. But smaller ingots often do solidify perfectly solid and without evolution of nitrogen; others evolve nitrogen.

These cross-sections (indicating samples) have been lying around the laboratory for a year or so, since the work was completed, and they are a little rusty, but here is one fairly solid and here is one with a large hole in it. I think this has silicon added and the evolution of nitrogen has produced quite a large cavity.

The dissociation pressure of iron nitride extrapolated from the results at lower temperatures obtained by the fixed-nitrogen research laboratory amounts to about

200,000 atmospheres pressure at the temperatures at which we were working. That would be the dissociation pressure of Fe_4N to form pure iron and nitrogen, but obviously we do not have quite such a simple thing because our Fe_4N is dissolved in iron and very much diluted. We can calculate dissociation pressure in the diluted state if we make some more or less reasonable assumptions in regard to what the solubility of Fe_4N might be in liquid iron, if you could hold it experimentally at 200,000 atmospheres pressure. Let us imagine, for instance, that we have a bomb capable of withstanding 200,000 atmospheres at 1600°C . and we put Fe_4N into it, and measure the solubility of Fe_4N in liquid iron. We might expect it to be fairly large, judging by analogy with Fe_3C and Fe_3P , and so on. If we assume it is completely soluble at 200,000 atmospheres and calculate its solubility at one atmosphere, it comes out about 0.05 per cent for the solubility of nitrogen. We found 0.04 per cent, which is not bad agreement with theory, if your theory is reasonable.

Perhaps it is the most reasonable theory to assume that the nitrogen is dissolved as a nitride, probably Fe_4N , possibly some other nitride, but certainly if Sieverts' law holds, a nitride containing one atom of nitrogen per molecule, regardless of how many atoms of iron may be present.

An explanation of how the nitrogen dissolved would certainly be a thing of importance. A study of the reaction of dissolved nitrogen, or Fe_4N , if you wish, with various elements, is important. We have made such a study and I may say in general that one surprising result of the experimental features of that study was that additions of aluminum did not prevent evolution of nitrogen, did not form any recognizable aluminum nitride in the metal, and entirely failed to agree with our predictions in regard to what its effects would be.

If we can ever study this thing by Dr. Hoyt's fractional method, we certainly should expect a great deal of light to be shed upon the general problem of nitrogen in steel. We know in a general way the order of evolution of CO from oxides in steel by that same method, FeO first, MnO next, SiO_2 next, Al_2O_3 next, with various others interspersed between.

I might venture to predict, Dr. Hoyt, a similar order for evolution of nitrogen. This is merely a guess, understand: iron, manganese, silicon, and aluminum, with zirconium and titanium both last; whether the zirconium or titanium will be ahead, I cannot predict.

R. H. SWEETSER,* New York, N.Y.—Would it be possible to make a similar test using pig iron, and to melt it, and is there any likelihood of having the nitrogen forming cyanogen with the carbon?

J. CHIPMAN.—I think the study in pig iron would be thoroughly possible and practicable. I do not know about the formation of cyanogen, but my guess would be that it would not trouble the investigation at all.

Originally we planned to study the effects of a number of alloy elements upon the solubility of nitrogen, and aluminum and silicon were slated for first investigation, after which we planned to go to chromium. And that reminds me of a thing which I wanted to call to Mr. Gottschalk's attention. The fact that nitrogen's solubility in iron is greater than its solubility in any of the other 21 elements of the International Critical Tables is not so very surprising because the knowledge of the solubility of nitrogen in chromium has not yet reached the International Critical Tables. The solubility of nitrogen in chromium has been determined with a fair degree of reliability, if not to say precision. Dr. Krivobok has made some very interesting experiments on that, which were reported last fall, and it is my recollection that he showed solubilities as high as 4 per cent of nitrogen in metallic chromium. I have made melts of metallic

* Consulting Engineer, Blast-furnace Practice.

chromium, not in nitrogen, but in air, ordinary atmospheric air, melting the chromium and casting it as rapidly as possible in a small induction furnace, so that the whole time of the heat was not over twenty minutes in a very small, high-powered furnace. The liquid chromium was exposed to atmospheric air for perhaps five minutes of that time, and the resultant metal contained 2 per cent nitrogen by weight. I do not know what per cent that is by volume at 1600° C.

R. H. SWEETSER.—I asked that question regarding the pig iron because in the Joint Committee on the Properties of Pig Iron there have been cases brought up in which there seems to be no difference whatsoever between two pig irons, one giving bad results and one giving good results, and it seems possible that this question of nitrogen may be the answer to it; and, if it is, our Committee ought to take it into consideration.

S. L. HOYT AND M. A. SCHEIL, Milwaukee, Wis. (written discussion).—The writers feel that there is a great deal of significance attached to the fact that nitrogen does not always occur as iron nitride in steels. As the authors of this paper quote, "the presence of nitrogen in steel has been repeatedly suggested to be due to the absorbing power of impurities rather than to the solubility of nitrogen in liquid iron itself." While this statement is general, there certainly are some experimental facts that indicate that titanium and zirconium are particularly good scavengers of nitrogen.

The authors have not shown that the absorbed nitrogen occurs as anything except iron nitride. For some time during our investigational work on gases in metals, we have observed definite nitrogen fractions, as described by Dr. Lewis Reeve¹³. That paper discusses the evolution of nitrogen and hydrogen at the various oxide dissociation temperatures and suggests that the nitrogen evolved comes from the thermal decomposition of a series of nitrides of increasing stability; requiring, therefore, higher and higher temperatures for decomposition. It is known that iron and manganese nitrides are easily decomposed at temperatures below 1000° C. and it is reasonable to assume that the nitrogen collected in the first fraction, at temperatures up to 1170° C. in vacuo, includes the nitrogen from these nitrides. With regard to other possible nitrides, it is stated by Jean Rieber¹⁴ that AlN decomposes above 1400° C., that TiN and ZrN decompose above 1100° C. N. Tschischewski and N. Blinov¹⁵ found that vanadium nitride begins to dissociate above 1300° C. and titanium nitride above 1500° C. Also, N. Tschischewski¹⁶ reports that manganese nitride begins to dissociate at about 1000° C., but indicates that silicon and aluminum nitrides are dissociated only at temperatures over 1400° C. and 1750° C., respectively.

Experimental data on these nitrogen fractions are illustrated by Table 1 of Lewis Reeve's paper. Four melts of ingot iron were prepared in a magnesia crucible heated by high-frequency current. The first melt was highly oxidized ingot iron and shows nitrogen only in the high-temperature fraction at 1570° C., from which we assume that this nitrogen is associated with aluminum. No nitrogen occurred at 1050° to 1170° C., indicating that there was no iron or manganese nitride. Melt 2 was oxidized ingot iron deoxidized with aluminum. This shows nitrogen in the low-temperature gas fraction and in the 1570° C. fraction, indicating that there are two different nitrides present. Melt 3 was oxidized ingot iron deoxidized with ferrosilicon. This shows

¹³ L. Reeve: Improvements in the Vacuum Fusion Method for Determination of Gases in Metals. *Trans. A.I.M.E.* (1934) **113**, 82.

¹⁴ Doctor's Thesis, Technische Hochschule, Hanover, 1930. Abstract in *Metals & Alloys*, 1932.

¹⁵ Titanium, Vanadium and Nitrogen. *Rev. soc. russe metall.* (1914) **1**, 636. *Chem. Abst.* (1916) **10**, 2685.

¹⁶ The Occurrence and Influence of Nitrogen on Iron and Steel. *Jnl. Iron and Steel Inst.* (1915) **92**, 47-90.

only one nitrogen fraction at 1300° C. and indicates that the nitrogen is associated with silicon. Melt 4 was oxidized ingot iron deoxidized with ferromanganese. The nitrogen is definitely associated with iron and manganese and aluminum nitrides. It is interesting to note that the only nitrogen associated with the silica fraction was evolved in the sample that was deoxidized by silicon.

We have experimental data showing quite clearly that nitrogen in weld metal is associated with deoxidizing agents such as silicon, manganese and aluminum. Reference is made to a weld metal made with a heavy slag-coated electrode; see Table 4, weld 6221-2 of Reeve's paper. The nitrogen associated with iron and possibly manganese amounts to 0.009 per cent; the nitrogen associated with silicon, 0.010 per cent and with aluminum, about 0.017 per cent. The composition of the slag coating of the electrode gives a manganese silicate slag which is deoxidized by a small aluminum wire wrapped in the coating. Commercial semi-killed steels usually show low total nitrogens of about 0.005 per cent. Often no nitrogen occurs in the 1050° to 1170° C. fractions, but does occur in the 1320° C. fraction and in the 1570° C. fraction, to suggest that the nitrogen is combined with silicon and aluminum.

We believe that nitrides of some composition, depending upon the particular deoxidizer used, are formed when nitrogen is absorbed by molten steel. It would be of particular interest to have the results of the fractional vacuum fusion method on some of the authors' melts, particularly those with 0.15 per cent Al and 0.7 per cent Si. A suspicion that ZrN may have been formed in a few heats could have been confirmed possibly by a method such as this, as the decomposition temperature is well above that of 600° C. for iron nitrides and 700° C. for manganese nitrides as given by Fry.

Finally, the correlation of fractional nitrogen determinations with the microstructure and physical properties is very fragmentary, but this field of investigation should yield interesting results.

A. SIEVERTS,* Jena, Germany (written discussion, translated by F. G. Norris). Before receiving a copy of the paper by Chipman and Murphy, we had submitted a

TABLE 2

| | Form of Iron | Temp., Deg. C. | <i>L</i> , Mg. N ₂ /100 g. Fe | $\Delta L/\Delta t$ |
|----------------|------------------|----------------|--|---------------------|
| A ₃ | Alpha | 750 | 0.4 | Positive |
| | | 890 | 2.0 | |
| A ₄ | Gamma | 900 | 25.0 | Negative |
| | | 1300 | 22.0 ² | |
| | | 1390 | 21.0 ² | |
| F _p | Delta (Alpha) | 1420 | 10 0 | Positive |
| | | 1450 | 11 0 | |
| | | 1500 | 12.0 | |
| | Liquid | 1540 | 31 0 | Positive |

report Iron and Nitrogen to the *Zeitschrift für Physikalische Chemie*. We are now sending a proof of this paper with some necessary additions, which I hope will serve as discussion material. We expect in the near future to try a direct determination of nitrogen absorption in liquid iron.

* Chemisches Laboratorium der Thüringischen Landesuniversität.

[The following is an extract from the paper by A. Sieverts and G. Zapf.]

An investigation of Fe-Cr alloys, concerning which we cannot yet report fully, involved the determination of the hitherto unknown dissolving power of Fe above 1200° for nitrogen. Armco iron turnings and nitrogen at atmospheric pressure were used. The absorption vessel consisted of pure aluminum oxide. The new results are compared with three old measurements in Table 2. The gas absorption and evolution takes place without hysteresis at 1400°. Thus, each modification of iron has its own particular solubility curve. Perhaps the δ curve may be regarded as the extension of the α curve. At the solidification point, 1530°, the solubility amounts to about 30 mg. N_2 in 100 grams of liquid iron, and 13 mg. N_2 per 100 grams of solid δ iron. Thus, during solidification in a nitrogen atmosphere 100 grams of iron is able to evolve 17 mg. of N_2 (13.6 c.c. at normal temperature and pressure, or 90 c.c. at 1530° and 760 mm.). Sawyer's observation of spitting during solidification is confirmed. He and other investigators have also estimated fairly

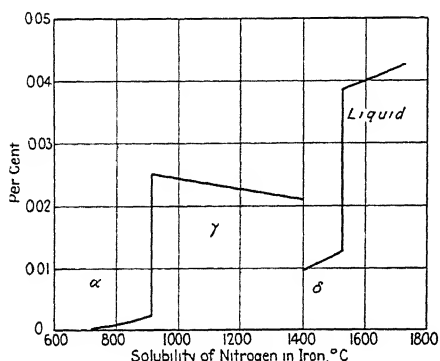


FIG. 6.

year. They have not measured the absorption of nitrogen by liquid iron immediately as we did, but measured the amount of residual nitrogen in the metal after solidifying and cooling in nitrogen at atmospheric pressure. Their value of 39 mg. N_2 per 100 grams Fe for electrolytic iron saturated at 1540° is about 25 per cent higher than ours. Because as yet for purely technical reasons we have been able to make only one determination of the dissolving power of *liquid* iron for nitrogen, a confirmation is necessary. This will probably lead to a decision between the two values.

J. CHIPMAN (written discussion).—Most of the points brought up by discussers have been mentioned in my oral discussion. Particularly I wish to thank Professor Sieverts for his contribution. The results of his splendid researches upon the solubility of nitrogen in solid iron now permit us to plot the entire iron-nitrogen system at atmospheric pressure as shown in Fig. 6. Three of the four sections of the solubility line are based upon the data of Professor Sieverts and his coworkers. In regard to the slight discrepancy between the two sets of data, I might suggest that this would be partly compensated by adding to Professor Sieverts' figure the 0.003 per cent nitrogen normally present in Armco ingot iron.

Metallurgical Effects Produced in Steel by Fusion Welding

BY A. B. KINZEL,* MEMBER A.I.M.E.

(New York Meeting, February, 1935)

PRECISE knowledge regarding the effect of heat treatment on the properties of steel has made possible the detailed specifications and instructions covering optimum heat-treating temperatures and practices that are in current use. A distinct contrast is presented by the metallurgical treatment of steel adjacent to a fusion weld, as such steel is subjected to each temperature from room temperature to fusion temperature, and cooled at a rate that is not generally controllable but is predetermined by the nature of the assembly to be welded, the kind of welding used, and the surrounding conditions. This is true regardless of the type of fusion welding: oxyacetylene, electric arc, thermit or flash resistance. Therefore it seemed desirable to investigate the effect of this metallurgical treatment on the characteristics of carbon steels commonly used for welding, by a detailed study of metal subjected to each temperature range; i.e., each heat-affected zone.

Oxyacetylene welding was chosen for the investigation because of the experimental facility of accurately segregating and studying each temperature zone. The nature of the zones produced by other types of welding is the same. The difference is primarily a matter of dimensions of each of the temperature zones involved. The advantages and disadvantages of the extent of the zone are of prime moment, and are discussed after the presentation of the detailed zone study. No mention is made of the fused metal proper, as this has been the subject of much published research and the nature of the solidified metal is fairly well known.

GENERAL METHOD

The scheme of procedure in the work herein reported involved the testing of the metal of each temperature zone adjacent to the weld in so

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* Chief Metallurgist, Union Carbide and Carbon Research Laboratories.

far as the usual physical tests could be applied to the small section available. This was followed by the synthetic preparation of specimens to duplicate the microstructure and the physical properties that could be

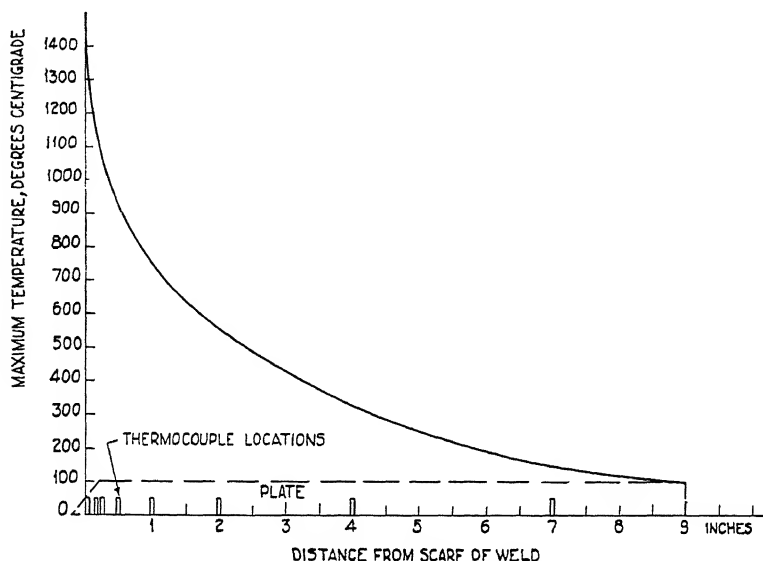


FIG. 1.—TEMPERATURE REACHED IN $\frac{1}{2}$ -IN. WELD PLATE DURING WELDING.

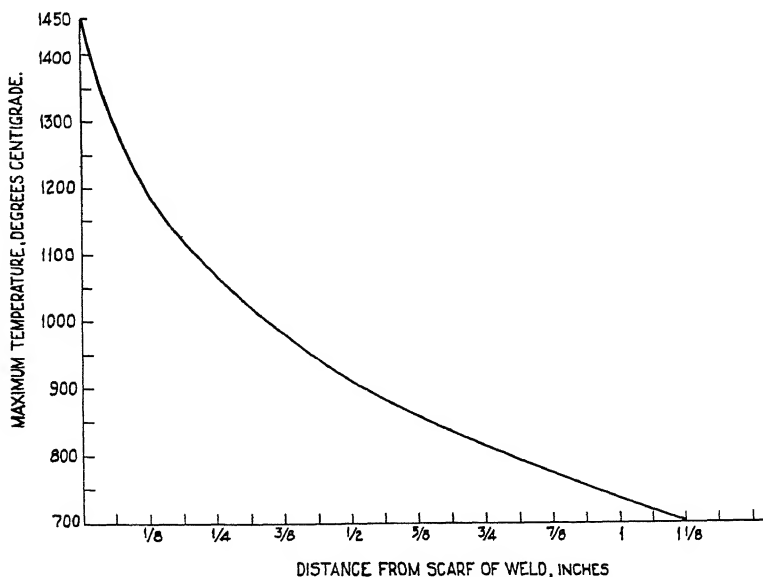


FIG. 2.—TEMPERATURE REACHED IN $\frac{1}{2}$ -IN. WELD PLATE DURING WELDING

measured on each of the small zones. Standard physical tests on the synthetically prepared specimens were then carried out and the values correlated. With each zone represented in this way, fairly complete

physical test data have been prepared, corresponding to the condition of each metallurgically affected zone adjacent to the weld.

EFFECT OF TEMPERATURES ABOVE 600° CENTIGRADE

It has long been known that when a piece of steel is welded the structure and physical properties of the material adjacent to the weld are

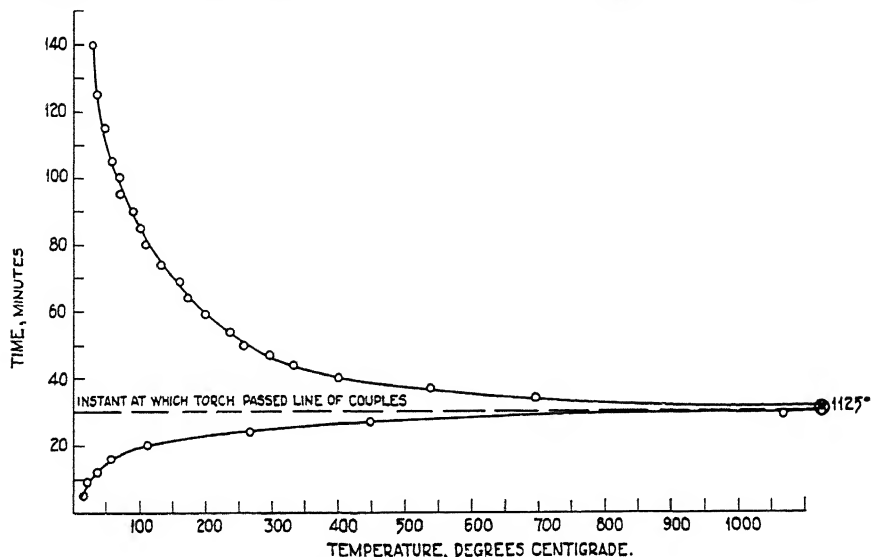


FIG. 3.—TIME-TEMPERATURE CURVE, POSITION 2.

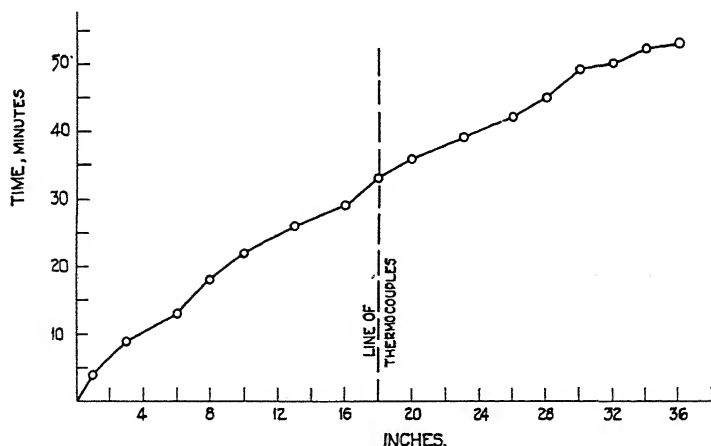


FIG. 4.—SPEED OF WELDING ON TEST PLATE.

altered by temperatures higher than 600° C. In order to obtain quantitative data, an oxyacetylene weld was made in $\frac{1}{2}$ -in. plate specially selected as high-strength firebox quality. This analyzed 0.24 per cent carbon, 0.41 manganese, trace of silicon, 0.02 phosphorus and 0.037 per

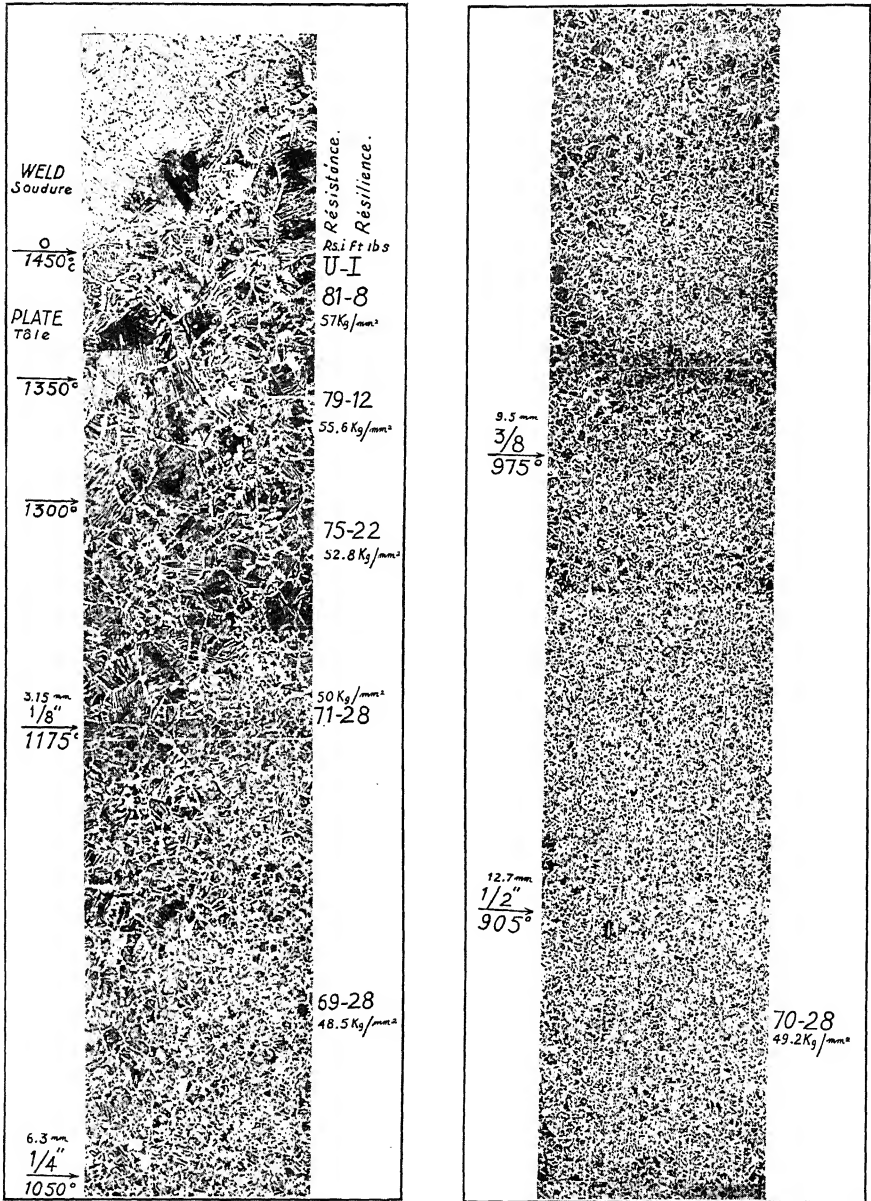


FIG. 5.—CONTINUOUS PHOTOMICROGRAPH OF PLATE ADJACENT TO OXYACETYLENE WELD.

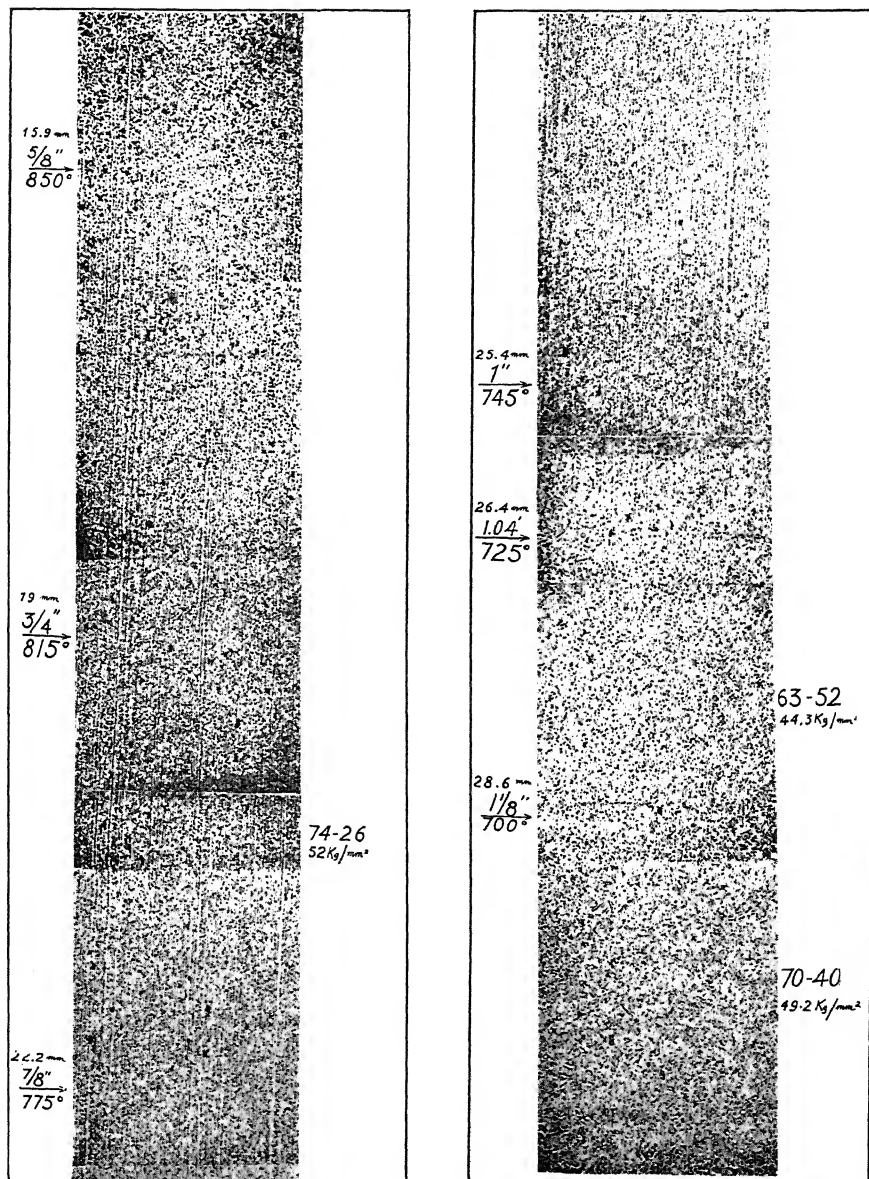


FIG. 5.—CONTINUED.

cent sulfur. The strips were 9 in. wide, with a 45° beveled edge on a 36-in. length. Thermocouples were placed on a line normal to the weld and equidistant from the ends of the weld. In each case a $\frac{1}{16}$ -in. hole was drilled halfway into the plate and the thermocouple was rammed into the hole with 200-mesh magnesite. Figs. 1 and 2 show the location of the thermocouples and maximum temperature reached as a function of the distance from the weld, the edge of the scarf being used as the zero point. Fig. 3 shows a typical heating and cooling curve as obtained with couple No. 2, and Fig. 4 shows the speed of welding. The difference of $2\frac{1}{2}$ min. at the line of thermocouples in Fig. 4 showing the rate of welding and the time shown for maximum temperature in the temperature curve (Fig. 3) is due to the preheating of the scarf.

The continuous photomicrograph (Fig. 5) shows the microstructure of the oxyacetylene-welded plate from the scarf back through the annealing zone, and the parallel zone in a similar plate welded with a heavy coated electrode is shown in Fig. 6. It is evident that the welding has decidedly altered the structure. The material that has been affected by the heat of welding may be divided into a number of zones, which are more clearly defined in the oxyacetylene-welded plate. First, the zone immediately adjacent to the scarf: this was at a very high temperature a very short time; the heat effect has produced a coarse-grained structure with pearlo-sorbitic grains in a ferrite network. Second, the zone immediately behind this, about $\frac{1}{8}$ in. from the scarf: here some grain growth is apparent but no network exists, although ferrite is the continuous phase. Third, the zone comprising the critical range: here the grain size is small and the banding, which is due to slight carbon segregation, is accentuated. Note the typical angularity of the pearlite in this zone. Fourth, the sub-critical annealing zone: this zone was held at just below the critical point and has softened because of the incipient spheroidization of carbide.

In order to determine the physical characteristics of the various zones affected by the heat, specimens taken from the same plate were heated to temperatures varying from 600° to 1400° C. in a gas furnace with an atmosphere maintained a shade on the carburizing side of neutral. The specimens were held at temperature just long enough to be heated through. The samples were taken from the furnace and swung in air until they reached about 500° C., after which they were held still. The microstructures of these samples were examined, and tensile and Izod tests were performed. A remarkable check on the temperature and microstructure of these special heat-treated samples and the zones in the weld plate was noted (Figs. 7 and 8). In addition, Rockwell readings were obtained on the cross-section of the welded plate, and corresponding readings taken on the specially treated samples (see Fig. 9 and Table 1). As a further check on the identity of the specially treated samples and zones in the welded plate, one section of the weld plate was cut into

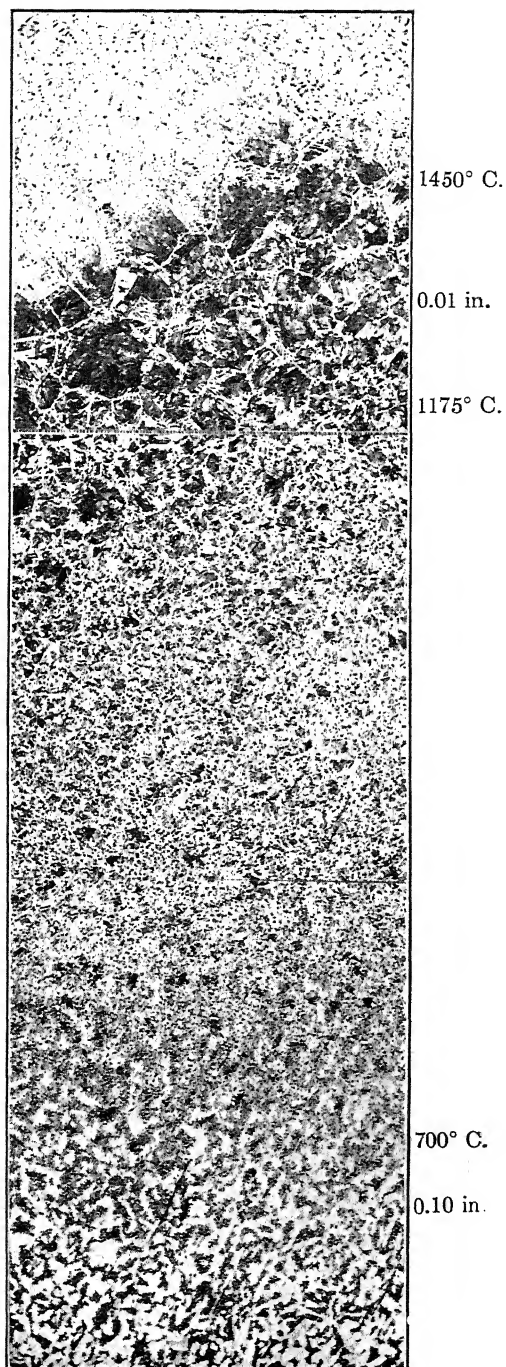


FIG. 6.—CONTINUOUS PHOTOMICROGRAPH OF PLATE ADJACENT TO HEAVY COATED ELECTRODE WELD.

slices $\frac{1}{10}$ in. thick, as shown in Fig. 10, and bend tests were performed on these slices. These were checked against results obtained on similar samples specially treated as previously indicated (Table 1).

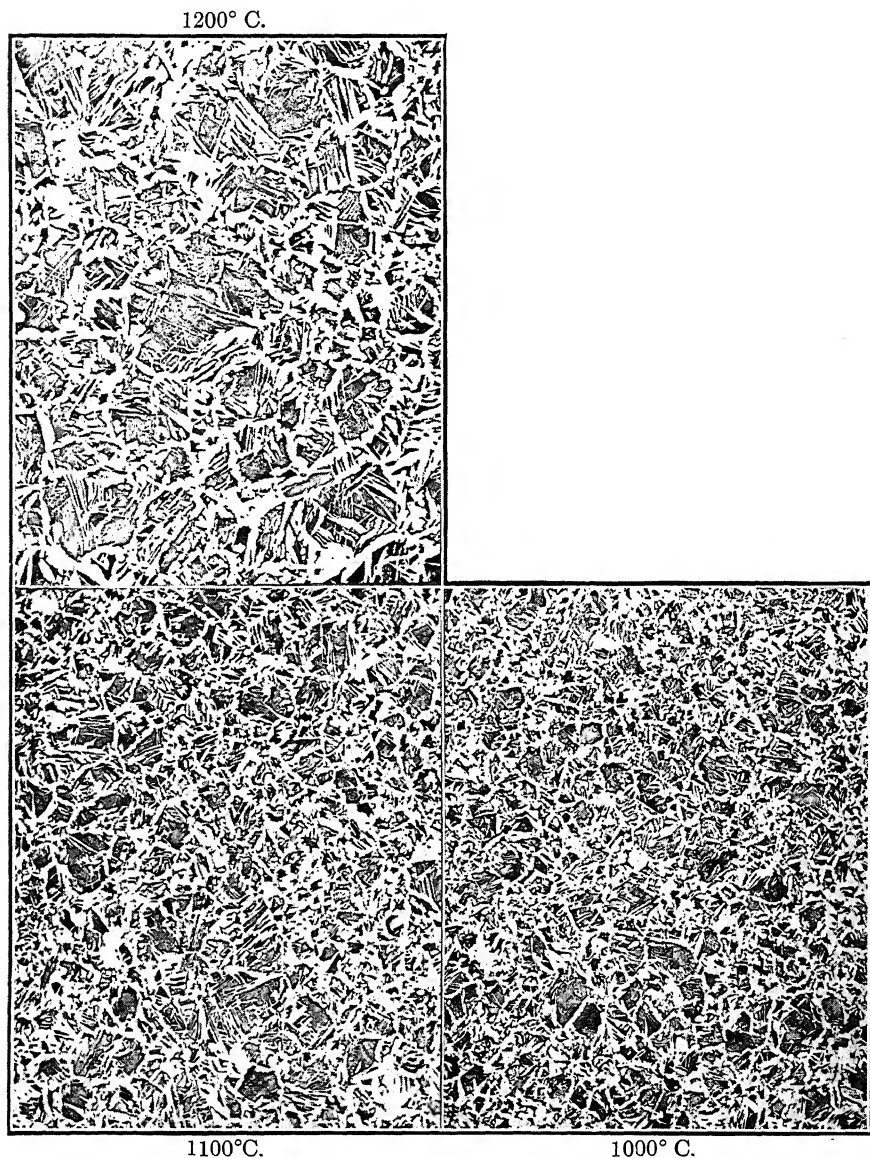


FIG. 7.—MICROSTRUCTURE OF SPECIAL FURNACE-TREATED SPECIMENS. $\times 100$.

Lest it be considered that the furnace atmosphere on heating has affected the shock resistance without affecting the other properties of the material, specimens were heated with the oxyacetylene flame and the

temperature read with an optical pyrometer. The microstructures of these specimens (Fig. 11) compared well with the furnace-treated specimens and the zones in the welded plate, and in all cases the resulting Izod

1400° C.

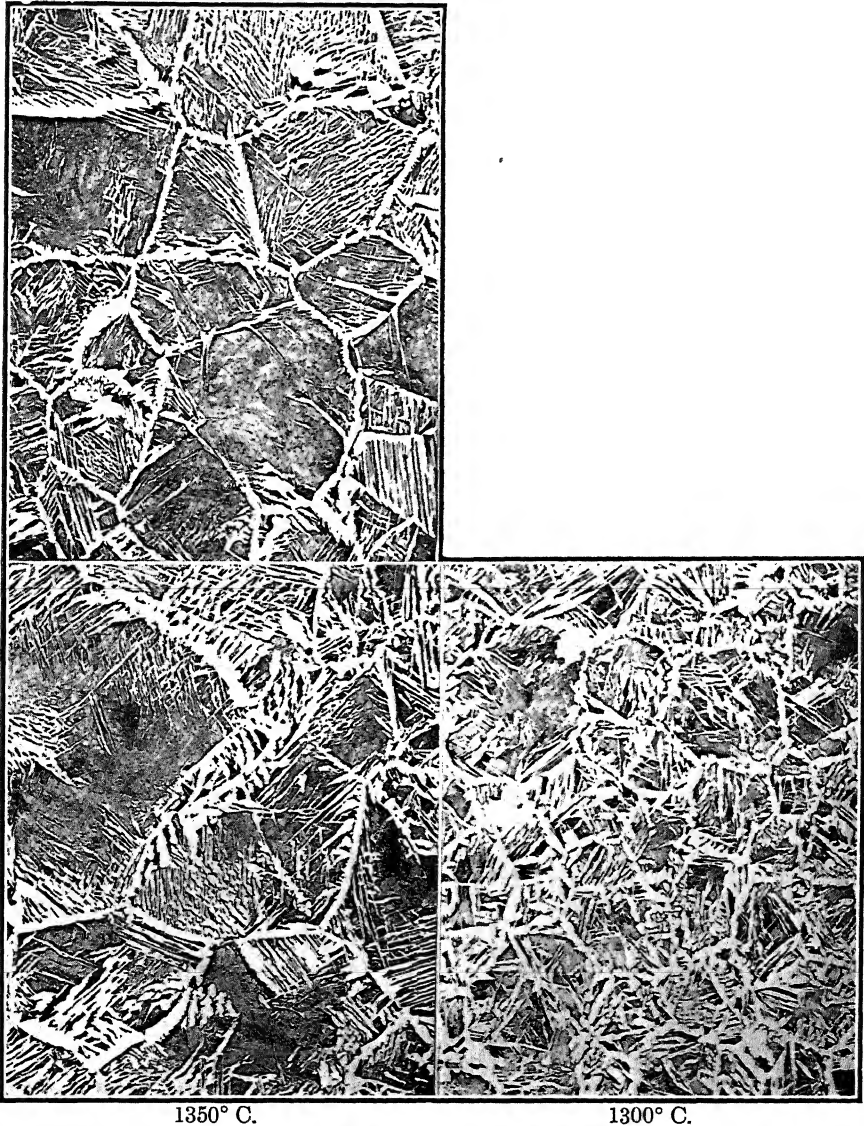


FIG. 8.—MICROSTRUCTURE OF SPECIAL FURNACE-TREATED SPECIMENS. $\times 100$.

value checked the Izod values of the specimens treated in the gas furnace (Table 1).

As the temperatures of heating, the microstructures, the hardnesses, the bend elongations, and heating atmosphere of specially treated samples

are identical with corresponding properties and attributes of definite zones in the welded plate, it is reasonable to suppose that the tensile properties

TABLE 1

| Specimens Taken from Plate Adjacent to Weld | | | | Furnace Heated Matched Specimens | | | | | | | |
|---|-----------------------------|---------------------|----------------|----------------------------------|---------------------|----------------|---|--|------------------------------|-----------------------------|-------------|
| Distance from Scarf, In. | Max. Temp. Reached, Deg. C. | Rockwell B Hardness | Bend, Per Cent | Temp, Deg C | Rockwell B Hardness | Bend, Per Cent | Yield Point, Lb per Sq In. ^a | Ultimate Strength, Lb. per Sq In. ^a | Elongation in 2 In. Per Cent | Reduction of Area, Per Cent | Ft-lb. Izod |
| 1/16 | 1405 | 82 | | 1400 | 82 | 11 | 46,000 | 81,000 | 14 | 16 | 8 |
| 1/32 | 1360 | 80 | 24 | 1350 | 81 | 28 | 43,000 | 79,000 | 19 | 31 | 12 |
| 1/16 | 1285 | 79 | | 1300 | 79 | Flat | 40,000 | 75,000 | 26 | 49 | 22 |
| 1/8 | 1185 | 78 | Flat | 1200 | 78 | Flat | 40,000 | 71,000 | 32 | 58 | 28 |
| 3/32 | 1090 | 76 5 | Flat | 1100 | 76 | Flat | 40,000 | 69,000 | 35 | 54 | 28 |
| 1/32 | 900 | 75 | Flat | 900 | 74 | Flat | 40,000 | 70,000 | 35 | 56 | 28 |
| 1/16 | 795 | 72 5 | Flat | 800 | 74 | Flat | 43,000 | 74,000 | 27 | 52 | 26 |
| 1/8 | 700 | 70 | Flat | 700 | 70 | Flat | 36,000 | 64,000 | 38 | 62 | 52 |
| Plate | | | | | 75 | Flat | 48,000 | 70,000 | 29 | 52 | 40 |

SPECIAL TORCH-HEATED SPECIMENS

| Temp, Deg C | Rockwell B Hardness | Yield Point, Lb. Sq In. ^a | Ultimate Strength | Elongation in 2 In., Per Cent | Reduction of Area, Per Cent | Ft-lb. Izod |
|-------------|---------------------|--------------------------------------|-------------------|-------------------------------|-----------------------------|-------------|
| 1350 | 82 | 41,000 | 78,000 | 20 | 36 | 14 |
| 1150 | 77 | 42,000 | 70,000 | 29 | 56 | 26 |

^a Average to nearest 1000 lb. per sq. in. of duplicate tests.

and Izod values of the specially treated specimens and the corresponding zones are also the same. Thus, we may accept the figures obtained on

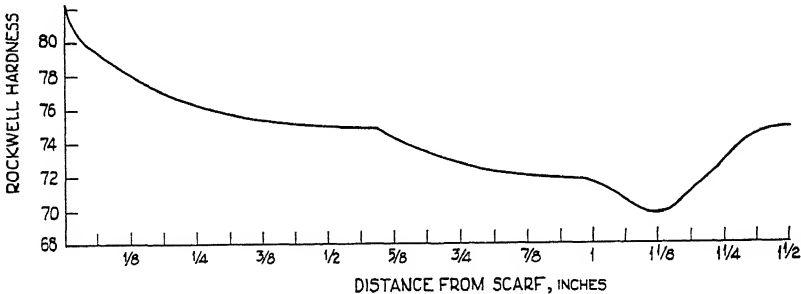


FIG. 9.—ROCKWELL READINGS ON WELDED PLATE.

the specially treated samples as representative of the zones in the welded plate. These figures are shown in the table.

From the consideration of these physical properties, it is evident that a significant change in the physical properties of the plate material has occurred in two zones only; i.e., one immediately adjacent to the scarf,

and one corresponding to the temperature just below the critical point. Accordingly, a specimen of the first zone was mounted in a specially constructed bending apparatus on the stage of the microscope, with the section in question under observation. The path of fracture could be noted with ease, and followed the grain boundaries. The high static strength of these grain boundaries corresponds to their lowered ductility, so that the combination is advantageous; that is, because of their high strength and because they are immediately adjacent to zones of lower strength and higher ductility, the material of this zone will not be stressed to a point at which the decreased ductility is significant. The other half of the same weld was then normalized at 900° C. for 5 min., and the corresponding section was cut out and bent in a jig. In this case the sample exhibited



FIG. 10.—METHOD OF CUTTING SLICES OF WELD PLATE.

characteristic slip planes, and bent almost completely upon itself without showing any signs of failure on the surface.

Investigation of the second zone referred to, namely, that which corresponds to the maximum subcritical temperature, shows a minimum strength only 10 per cent lower than that of the plate proper. In the instance in question, this occurred 1.04 in. from the scarf, and runs approximately parallel to the line of the scarf. Therefore it is not in a direct line of tensional stress, so that in testing welded structures with tension stress normal to the weld, the decrease in maximum tensile strength obtained on test specimens will generally be less than 10 per cent and may be negligible. This is further borne out by experience in testing thousands of welded joints where the minor factors in testing have resulted in failure of the plate in a zone further removed from the weld than the subcritical temperature zone herein discussed, and at approximately specified plate strength.

The extremely high ductility of this zone deserves special mention, in that with such ductility material may be used with a greater ratio of design fiber stress to ultimate strength. A quantitative evaluation of this ratio is difficult, but that the improved ductility would allow at least a 10 per cent increase in the design fiber stress based on the ultimate strength and present factor of safety is common engineering judgment. Thus, from the engineering service standpoint, this material is fully the equal of the steel metallurgically unaffected by the welding process. Normalizing completely eliminates the zone in question.

EFFECT OF TEMPERATURES UP TO 600° CENTIGRADE

It is common knowledge in the metallurgy of steel that the tempering effect of temperatures between 600° C. and the critical temperature is much more pronounced than that of lower temperatures. Moreover,

because of the short time involved, the microstructure of the zone up to 600°C. could not be differentiated from that of the initial plate, and the hardness tests on the plate proper and on the metal in the 550°C. 1300°C.

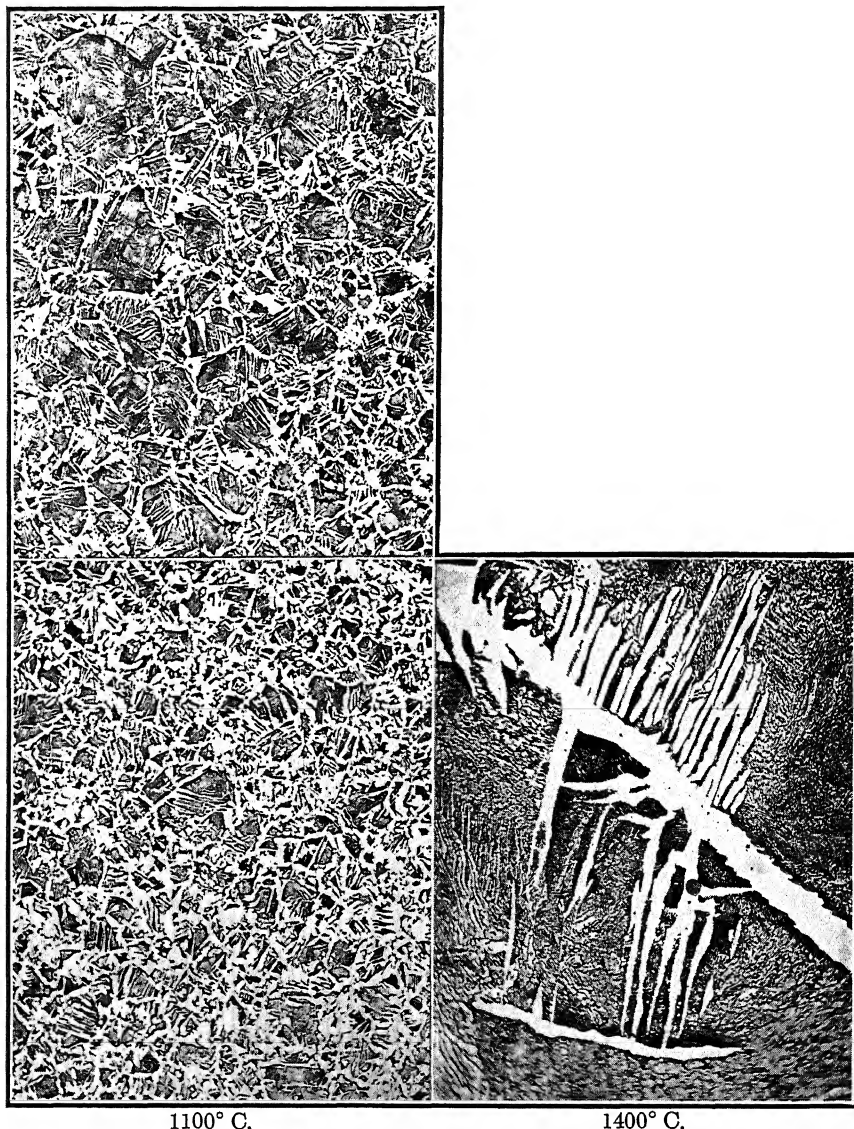


FIG. 11.—MICROSTRUCTURE OF SPECIAL TORCH-TREATED SPECIMENS ($\times 100$) AND OF COARSE STRUCTURE ADJACENT TO SCARF ($\times 500$).

temperature zone showed identical values; namely, Rockwell B-75. Thus for the purpose of this study, it may be considered that the purely tempering effects of temperatures up to 600°C. may be neglected.

For the sake of completeness, the phenomenon known as temper brittleness or blue brittleness should be mentioned. It is generally recognized that holding at temperatures in the general vicinity of 400° C. renders many steels brittle without causing a perceptible change in the microstructure. An experimental check of the 400° C. zone failed to show any change in impact strength as against that of the plate proper because the time at temperature necessary for this phenomenon to occur is of a much greater order of magnitude than that encountered in the welding operations. Accordingly, this matter need not be given further consideration.

Plate for welding is often strained. In welded structures such as pressure vessels, an appreciable amount of cold work is frequently done on the material before welding; for example, in 1-in. plate bent to a 50-in. diameter circle, a strain of 2 per cent is produced in the outer fibers. It is generally recognized that in some classes of steel this strain followed by room-temperature aging produces decided brittleness in the steel. Moreover, such brittleness has been noted in welded plate far from the weld and in plate prior to welding. As aging takes place at room temperature, strain age brittleness should not properly be regarded as due to the heat effect of the welding operation as far as the production of aging is concerned, and it should be emphasized that the phenomenon is common in riveted structures. Moreover, in many types of welding the internal stresses produced are not sufficient to cause brittleness in combination with subsequent aging at room temperature. As this is not always true, there is a definite basis for the statement that strain age brittleness in a welded plate may be related to the welding, and the phenomenon has accordingly been studied and the results here presented.

Specimens of the plate originally mentioned were strained 3 per cent in the tensile testing machine, and this was followed by a 24-hr. aging at 150° C. These seemed to be optimum conditions for the production of the brittleness. Izod values running 37 to 44 ft-lb. in the plate as received were reduced to 8 to 12 ft-lb. by the strain-aging treatment. The tensile strength was unaffected. To determine the effect of the amount of strain before aging, specimens were strained from 0.5 to 12 per cent, aged, and tested for Izod values. This showed definitely that with 1.5 per cent strain or more, brittleness invariably resulted from aging this plate, and that with less than this amount it occurred sometimes but not invariably. A study of the effect of variations in aging showed that one month at room temperature produced the brittleness after the standard 3 per cent strain. At 100° C. aging was readily produced in 1 hr., and at 200° C. in 5 min. Aging was likewise produced at temperatures up to 400° C. but not at higher temperatures.

Next experiments were performed to determine methods of removing the strain-age brittleness in this steel. It was found that heating for

periods up to 6 hr. at temperatures up to 450° C. did not affect the brittleness. Three hours at 475° C. raised the Izod values from 8 to 16 ft.-lb., but longer time at 475° C. did not further improve the Izod values. It was further found that 1 hr. at 525° C., or 5 min. at 550° or 575° C., brought the Izod value up to about 20 ft.-lb., and that 1 hr. at 550° C., or 5 min. at 600° C., brought the Izod value up to its full former value—40 ft.-lb. Samples normalized after strain brittleness also showed high Izod.

In most cases of important welded construction, a stress-relieving treatment is used corresponding to that shown to be effective for the elimination of the strain-age effects. It should be emphasized, however, that the strain produced in a continuous member is generally distributed throughout the member and is not necessarily restricted to the local zone in which the stress has been produced; that is, assuming a restricted member with internal stress set up at a given point, the stress is transferred throughout the member and may cause strain in excess of the proportional limit of the steel at any point in the member. Thus, local stress relieving or normalizing is not necessarily a remedy that will eliminate internal stress to the degree required to prevent strain-age embrittlement, and is not the equivalent of stress relieving the entire structure. However, normalizing for the purpose of grain refinement may be carried out locally without disadvantage, because the zone that is to be affected by the heat treatment is local in character.

EFFECT OF TEMPERATURE GRADIENT

The effect of local heat on steel is to produce internal stress due to temperature gradients, and the greater the magnitude of the temperature gradient, the more severe the internal stress produced; that is, a temperature drop from the melting point to room temperature, occurring in $\frac{1}{4}$ in. of steel, as indicated in Fig. 6, produces greater internal stress than a similar temperature drop in $2\frac{1}{4}$ in. of steel, as indicated in Fig. 5. This is not only evident from direct experience with different types of welding, but is in accord with general metallurgical experience. Two factors are constantly involved: (1) The setting up of stresses due to the volume change produced by the temperature gradient and the transformation that takes place in the steel on cooling, and (2) the relief of stresses due to the existence of a temperature zone from about 500° C. to the critical temperature. With a very steep temperature gradient, the quenching effect of the cold mass of the steel back of the heat-affected zone is such that the transformation on cooling occurs at a relatively low temperature, thus decreasing the extent of the temperature zone above 500° C. available for stress relief. Also, with a steep temperature gradient the extent of the zone from 500° C. to any given higher temperature, and the length of time it is available, are very much less than with a more gradual

temperature gradient. Once a structure as a whole is stress-relieved, the effect of the stress produced by the temperature gradient is eliminated, but consideration should be given to the possibility of permanently injuring the structure before such stress-relieving treatment is applied. Such permanent injury may, at the worst, take the form of a crack visible to the eye. It may be an internal crack discernible only by special testing methods, or it may consist of micro-cracks so small as to be discernible only under a microscope of the highest power, if at all, and yet constitute regions in which fatigue and impact strength have been markedly reduced. Such a condition may not be restored by a stress-relieving treatment. Naturally, the probability of encountering this type of phenomenon is greatly reduced when temperature gradients of less magnitude are produced in the welding operation. Preheating the entire member to be welded in one way to eliminate the steep temperature gradient, but experience and data gathered to date indicate that the temperature gradients encountered in oxyacetylene welding are of sufficiently low magnitude so that such practice is not necessary.

CONCLUSIONS

1. The heat of welding produces no noteworthy metallographic effect except in the zone immediately adjacent to the scarf. In this zone, the ductility is reduced, but the tensile strength is increased. If desired, this zone can be completely eliminated by local normalizing.

2. The minimum tensile strength in a welded joint exists in the zone subjected to the maximum subcritical temperature. This zone is not necessarily effective in reducing the strength of the joint as a whole. The high ductility of this zone, combined with the small decrease in tensile strength, permits its engineering use at the same fiber stress as that of the plate proper. This zone can be eliminated by general normalizing.

3. Commercial plate used for welding purposes is generally susceptible to strain-age brittleness. This may be produced by cold-working the plate before welding, or by internal stress due to the combination of restraint and steep temperature gradients in the welding operation. This can be completely eliminated by general stress relieving.

4. Steep temperature gradients may do permanent damage to the welded steel. The problem does not exist for procedure-controlled oxyacetylene welding, as such steep temperature gradients are never produced. In some other types of welding, the deleterious effect can be avoided to some extent by proper design.

ACKNOWLEDGMENT

The author wishes to express his appreciation of the cooperation in this work by Mr. J. R. Dawson and other members of the Union Carbide and Carbon Research Laboratories, with particular mention of Messrs. J. J. Egan, W. D. Forgang, J. R. Vilella and R. L. Wagner.

DISCUSSION

(Eric R. Jette presiding)

G. E. DOAN,* Bethlehem, Pa. (written discussion).—The act of fusion welding involves melting, oxidation and nitriding, casting and deformation of the weld metal, as well as heating, quenching and deformation of the metal adjacent to the weld. Certainly this array should attract the physical metallurgist to study welding problems. The author of this paper has devised a new and ingenious set of experiments to determine the effect of welding on the members joined, and in addition has focused the light of the best metallurgical knowledge upon the secondary results, such as temper brittleness and strain aging, which may accompany it. The publication of these results is a distinct contribution to the progress of the welding art.

The results of simulative tests in Table I show relative brittleness beginning about one inch from the weld with Izod 26 and increasing rapidly from 22 Izod at $\frac{1}{16}$ in. below the weld to 8 Izod $\frac{1}{64}$ in. below the weld, the original plate being 40 Izod. It would be interesting and informative to extrapolate beyond $\frac{1}{64}$ in. and estimate the brittleness at the weld itself; that is, at "zero" distance from the weld. Probably the Izod value would be quite low, as it is falling rapidly at $\frac{1}{64}$ in. The bend values, elongation and reduction values likewise are falling rapidly in this region if these simulative tests can be trusted. The rise in yield point and ultimate strength do accompany it, of course. I am not sure that I agree with the author on the whole, however, that the combination of high strength and low-ductility is advantageous, although the strength is to some extent a palliative for the low ductility.

Concerning the high ductility of the zone heated just under the critical temperature, he remarks that the metal of higher ductility here may be used with a greater ratio of design fiber stress to ultimate strength. I should like to ask how this ratio will change for the *low* ductility area mentioned above.

Finally, the author points out that steep temperature gradients and the accompanying stress gradients may do permanent damage to the steel. He gives two well conceived reasons why a steep gradient may be more injurious than a gentle one. Both are based on the fact that the cushion of plastic metal that can absorb the change in volume from austenite to pearlite is thinner with the steep gradient. But I should like to ask whether a gentle gradient does not counteract, at least partly, its own advantages by the fact that it requires a much larger volume of metal to be heated.

When this larger volume of heated metal cools, it will involve larger total expansion due to pearlite formation and larger total shrinkage due to cooling. The thicker cushion of hot metal may alleviate these larger readjustments, which are necessary with the gentler temperature gradient, but the author has not shown that it neutralizes them. With the steep gradient, the cushion may be thinner, but so also are the volume changes less.

S. L. HORT,† Wilwaukee, Wis.—I believe a person would be likely to get the impression upon reading the first paragraph and upon examining the photographs that the coarse-grained, overheated structure is a more or less common characteristic of fusion welding, regardless of the type, whether it be oxyacetylene, electric arc, and so forth. The point I wish to make here is that it does not apply to the multi-pass electric arc weld when it is properly made.

Last fall I read a paper on the metallurgy of arc-deposited weld metal¹, and one photograph in particular shows the transition from the weld deposit proper to the

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¹ The American Society for Metals, Fall Convention, 1934.

refined stock. That photograph shows how difficult it may be to detect any sharp line of demarcation. Actually under the microscope it is commonly quite puzzling to decide where the line of demarcation actually comes. Except for metal immediately under the top pass, the grain refinement at the junction between weld metal and plate stock is certainly all that can be desired, and it seems to me that if this paper does create the impression that all fusion welds have the overheated zone adjacent to the weld band, that impression should be corrected.

The next point relates to conclusion No. 4, which states that the steep temperature gradients may do permanent damage to the welded steel. Metallic arc welding involves steep temperature gradients and though the author does not say they necessarily do permanent damage, he says they *may* do permanent damage. I believe it should be pointed out here that when welding is properly carried out, there is no need to worry about this effect.

My general impression of the paper was (and I should like to ask Mr. Kinzel if this was the one he intended to give) that it was meant to raise points that are of great interest to metallurgists and bound to excite their curiosity, so much so that they will be made to think about them.

H. H. LESTER,* Watertown, Mass.—Were hardness measurements made adjacent to the weld? I ask that because in some of the work that we have been doing at the Watertown Arsenal with electric welding in alloy steel, we find in this overheated zone distinct increases in hardness. The hardness sometimes runs as high as 750 Brinell. On multiple-pass welding this hardness does not run as high; nevertheless, it is still there.

In weld on plain carbon steel there always is this hardened zone adjacent to the weld though hardnesses are not as great as with alloy-steel welds. Cracks sometimes develop in this hardened zone. We have tried giving the welds various treatments around 600° C., and after this stress relieving we find that there is still a hardness peak. It is not as high, of course, but it is still present. Probably at least part of the hardness in the zone is due to precipitation effects.

Some idea of what is happening may be obtained from observations made on poor arc welds in plain carbon structural steel. Under the microscope there was a large grain structure, but the metal was much harder and was also much stronger than would be expected from the compositions and grain size. We have attributed the effect to the absorption of nitrogen with subsequent precipitation of iron nitride.

Another thing we are interested in, some work that is in progress now, is the stress distribution adjacent to the weld in the heat-treated zone and on out into the plate. Have you any measurements of the stress distribution continuously away from the weld and out into the plate?

Another question: What is the effect of local stress relieving? Dr. Kinzel stated that it is better to stress-relieve the whole piece. We find that that is absolutely necessary for best results but what happens if you have a local stress relief instead of a general stress relief? Do you accomplish any relief adjacent to the weld?

W. E. BUCK,† Granite City, Ill.—I should like to ask the author if he has noted any difference in the stress zones due to the initial grain structure of the steel, that is, a steel in the as-rolled condition against an annealed plate.

A. B. KINZEL.—Naturally, in a paper of this type a certain amount of speculation is inherent. The object of the paper was primarily to focus attention on the various

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† Metallurgist, Granite City Steel Co.

points that must be considered, so that the very best possible welding of all types will be given to the industry. It was written for the metallurgists.

As to the low impact zone, next to the weld; by extrapolation from $\frac{1}{64}$ in., one can get a lower figure than 8 ft.-lb., but taking the weld itself at 16 ft.-lb., and performing extrapolation from that, one finds that the two curves intersect and that the minimum impact strength is not very much below the 8 ft.-lb. quoted in the paper. In this particular case, a 22 per cent carbon steel was used. With lower carbon the impact value would be higher, and low-carbon steel is more generally used in practice. Steel with the higher carbon content was chosen to emphasize the results.

The matter of design stress is a pertinent question. The design is based on the ultimate strength, although yield point may be used, and when all is said and done, both yield point and ultimate strength are taken into consideration. The factor of safety that is applied assumes that the other properties of the material are known. When there is a zone that would cause failure under a static load before failure would occur elsewhere, even though it be at a load very slightly under the average strength of the structure as a whole, it is necessary to justify the existence of that zone, and the fact that we can use it in service. The annealed zone is such a case, and, because of its ductility and service experience, a slight modification in the factor of safety is permissible.

Considering the zone with the lower ductility, one may say, "Why not apply the same reasoning?" Two reasons—first, if stresses are applied to the structure, they can not reach high values in this zone, because it is very narrow and surrounded by zones of lower strength and higher ductility. Thus the stresses cannot be distributed in such a way as to require high plastic deformation in this very narrow zone. Because of the extreme narrowness of the zone, and the fact that it lies on the high side rather than the low side, of average yield point and ultimate strength with reasonable shock resistance it renders adequate service. That reasoning has been checked by experience, many times; even with local bending moments present. It is possible that if this zone were located exactly at right angles to the axis of the plate, the effect might be different; but it is invariably at quite an angle.

As to the effect of extent of the zone above the critical temperature, with respect to that below the critical temperature, theoretical proof is wanting and it is necessary to fall back on our experience. Locked up stresses, internal stresses, are known to be low under these conditions, from measurement and from experience. Thus it would seem that the theory as presented at least matches our experience. Just why it cannot be reasoned that the larger zone above the critical temperature should more than offset the zone below the critical temperature again requires some close attention.

I believe that what happens is that this zone goes through the critical temperature at progressive intervals of time, continuously but progressively, and that at the time that any layer is going through this transformation the metal immediately adjacent thereto is plastic, so that a transformation wave occurs and the thing that determines to a large extent the degree of locked up stresses is the temperature distribution at the end of the wave.

In Dr. Hoyt's question regarding the microstructure, he pointed out that in the layer or multi-pass type of welding the microstructure next to the weld is not as coarse. That is perfectly true, because in applying a subsequent layer, the previous one is normalized. In the paper we have pointed out that local normalizing does eliminate this microstructure. However there is always the last layer. If this is not normalized in some way, a large grained structure will be evident as Dr. Hoyt has pointed out, so there is no point of disagreement. I am glad he emphasized that fact and I will repeat what I said a few minutes ago. The purpose of the paper is to point out the factors that should be given attention by the manufacturing metallurgists in the welding shop.

As to the possibility of permanent damage, the conclusions are carefully worded, but we do know of some instances in which such permanent damage has occurred. I should say that this matter is not a cause for alarm, but rather a cause for study of any individual welding problem by competent engineers and metallurgists before welding is undertaken.

The aging phenomenon mentioned falls into the same category and I might mention that every riveted vessel ever made, with few possible exceptions is subjected to strain aging. They all have lower ductility either locally or generally, and they all have given good service within limits, so that again there is no cause for alarm but cause for attention. A hardness curve was given in the paper (Fig. 9).

I wonder if the steels with which Dr. Lester has been working entirely correspond with the metals in general use in the industry today. They are alloy steels very much higher in carbon, in which the air-hardening characteristics are accentuated, and require particular attention.

As to whether or not there is a precipitation next to the weld, it certainly looks as if there were, because it is the only way to explain a structure apparently ferritic yet with very high strength. There may be another explanation but that is the easiest assumption.

As to the internal stress distribution; that is a problem that comes down to a particular weld. To generalize, perhaps we can say that in long welds, in plate, there is such and such a stress distribution. That problem has never been studied adequately. But even if we have an answer to that problem, we are still in a position where we want to know about any given case and we are going to have to improve our methods of studying the existence of internal stress. The methods now available are not adequate.

As to local stress-relieving, Dr. Lester mentioned that he would not use it. Again the problem has not been sufficiently studied, but there is sufficient evidence available to show that it needs study very badly and it is perfectly possible that local stress-relieving does more harm than good. We do not have the answer.

I know of no studies that have been made on whether or not the condition of the plate before welding is a factor, with the purport of answering your question. Naturally, because of the short time involved, only a slight difference, due to solubility of carbon, would be expected and the state of the microstructure before welding should have an effect on the resultant structure. Certainly this is true in the lower temperature zones. However, I think it is also true that while the effect undoubtedly will be there, the magnitude thereof and particularly the correlative physical properties, will not be markedly different, and from experience we can say that the difference is not of a major order of magnitude.

Wrought Iron in Today's Industrial Picture

BY JAMES ASTON,* MEMBER A.I.M.E.

(New York Meeting, February, 1935)

A PROPER consideration of this subject is not confined to the technical channels of production and metallurgy. It concerns an industry, and should cover economic aspects which are of material importance in any program of development. The discussion may logically be treated under three subdivisions, as follows: (1) manufacture, (2) characteristics related to quality of material; (3) adaptability and exploitation of product.

MANUFACTURE OF WROUGHT IRON

The manufacture of wrought iron is the most ancient art of the ferrous metal industry. The eighty years or less of existence of processes identified with our modern "Age of Steel" is a relatively brief interval compared with the several thousand years associated with the production of wrought iron by man. From the primitive early methods of production, manufacture for many centuries followed the line of direct reduction. There were developments as experience was gained through the years; but man's needs for a strong, ductile, forgeable product were met by reducing the ore to metallic iron in a single-stage operation.

Following the development several centuries ago of what has become our modern blast-furnace operation, manufacture of wrought iron was gradually transformed into a two-stage method of first producing cast iron and then refining this to the desired degree of forgeability; the forerunner in principle of today's scheme of manufacture of steel. The product retained the essential characteristics of highly refined base metal with iron-silicate slag incorporation, which were associated with the material resulting from direct reduction methods. Cort's invention of the puddling process in 1784 is a landmark in wrought-iron manufacture. It consisted essentially in adapting a coal-fired reverberatory furnace to the refining operation; thus lifting the industry out of the slough of

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dependence upon charcoal fuel, and greatly expanding the productive possibilities and uses of wrought iron. With Hall's improvement in the form of a basic iron oxide bottom instead of the sand hearth of Cort, we have in all essential features the puddling process, which was the almost sole reliance of man for a malleable ferrous product up to the bessemer invention of 1855; and which has been until very recently the method upon which wrought-iron manufacture was almost entirely based.

Scrutinizing the long history associated with the manufacture of wrought iron, one notes that there has been no set adherence to a particular method; the over-all period has seen numerous changes and developments, some of which have been quite radical in comparison with preceding practices. However, modern metallurgical knowledge has shown that the product throughout all of the past has maintained certain fundamental characteristics, regardless of transition in method of manufacture. Purity of base metal, and more particularly the inclusion within this matrix of an iron-silicate slag, have been basic distinctions of wrought iron in contrast with other ferrous metal groups.

For almost the entire period of history, or more specifically, until the attainment of high temperatures were available through the inventions of Bessemer and of Siemens, it appears evident that what we now class as wrought iron was the result of temperature limitations, with the result that solidification of the refined base metal took place in contact with the liquid slag. Mixture of the two was an inevitable result. The inherent characteristics of wrought iron which are today well recognized by the metallurgist were the natural result of the operation as conducted, and not because they were the focus of attention of the artisan. His objective was solely the production of a material having the forgeability and other physical properties desired by the consumer.

It appears beyond contradiction that the efforts of Bessemer and Siemens were not to displace wrought iron as a commodity, but rather to put manufacture upon a larger and less costly basis. Metallurgical science at the time had not developed to the plane that the anatomy of metals was understood; and it is quite evident that the inauguration of steelmaking processes was intended to produce a material satisfying the physical characteristics that the engineer was obtaining in wrought iron. With manufacturing success assured as the bessemer and open-hearth processes developed, there was logical expectation that puddling would fade into oblivion. That it has persisted to the present day in spite of obvious disadvantages in manufacture is due to a recognition that for certain services wrought iron has a performance record warranting its use in the face of necessarily higher costs and limitations of output. The puddling process remained because the now well-known anatomical characteristics of wrought iron were not obtainable at the time by other and better methods of manufacture.

Tradition has thrown a halo around the puddling process. It has had a commendable record for the production of quality wrought iron. To the extent that this result has been achieved, it is entitled to a full measure of credit. However, it is the conviction of the writer that, provided the goal of quality is reached as measured by well recognized standards to be enumerated later, the process of manufacture is a secondary matter. The degree of success to be attributed to any process for the manufacture of wrought iron should be gaged by the extent to which quality specifications are met, by the control and flexibility in operations, and by the engineering and economic aspects of production.

Much energy has been expended in attempts to displace puddling or the manual effort involved therein, with some more efficient or economical process. The earliest attempts lacked the refractories, engineering accessories, and technical knowledge necessary to give an even chance of success. In the middle period, the incentive was smothered by an attitude of hopelessness of the wrought-iron industry against the inroads of steel. In later years interest was revived, and progress was made; that the progress was slow or that it did not reach the ideal sought may be ascribed in part to misdirected effort; but in considerable degree it reflects the difficulty of the problem.

The more general attention has been given to so-called mechanical puddlers; machines intended to agitate the metal bath during refining, in simulation of the effort of a puddler in rabbling a heat. It is not the purpose of the writer to go into a critical discussion of mechanical puddling; it is sufficient to state that the handicaps and difficulties are great. Mechanical puddlers represent a group effort in one general direction, and success, individually or collectively, should be gaged not because of mechanical agitation of the bath or because of simulation of hand puddling; but because the wrought iron produced will meet all of the specifications, technical and economic, which are linked up with quality and the needs of engineering applications.

It has been the privilege of the writer to present papers before this Institute on two previous occasions on the general subject of wrought-iron manufacture. The first, in 1926, comprised an analysis of the problem and the results of experimental efforts toward a solution; the second, in 1929, described the evolution of the experimental phase into a plant of commercial size, then over two years in successful operation. At the time when that plant of the A. M. Byers Co., at Warren, Ohio, had fulfilled its primary exploratory function, output was well in excess of 200 tons per day. The pouring of the refined metal into the liquid slag, commonly referred to as "shotting," and which is the crux of the process and the key to the mechanism of disintegration, was at a rate of one ton in three minutes. The size of bloom produced was from one ton to 2500 lb. in weight.

As stated in the second article mentioned, the Warren plant was the proving ground and forerunner of the works now in existence at Ambridge, Pa., in the Pittsburgh district. In starting the Ambridge plant all of the general fundamental features of the Warren operation were retained. Changes in operating details and in other essential features were from time to time put into effect at the Ambridge plant, based in part upon the enlarged scope of operations and the experience gained in the earlier activities.

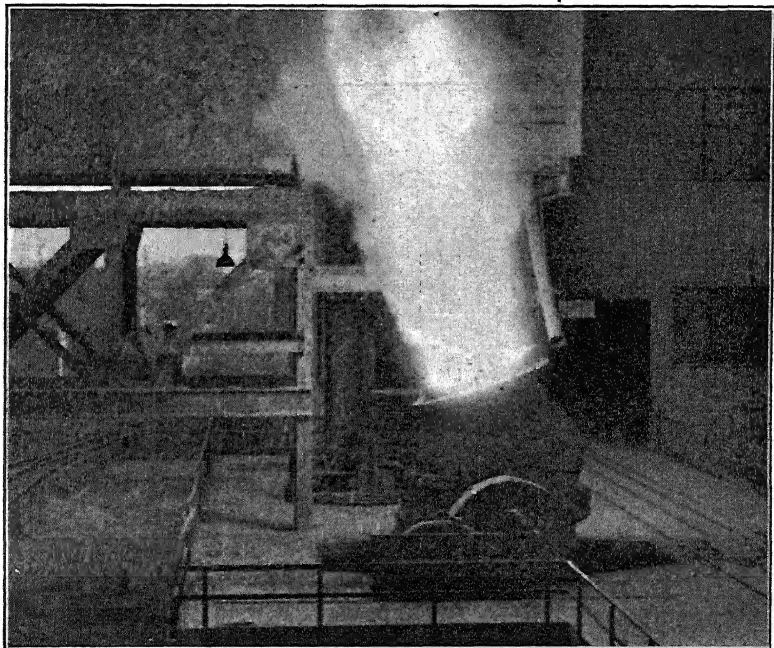


FIG. 1.—THE BESSEMER CONVERTER REMOVES THE IMPURITIES FROM THE MOLTEN IRON.

Pig iron is melted in cupolas and refined to the low metalloid content of a "full blown" heat in 10-ton bessemer vessels. Ultimately it is expected that the blast furnace will displace the cupola, with all of the advantages accompanying hot-metal supply to the converters. Desulfurization is effectively accomplished with soda ash in the cupola metal-transfer ladle, so that a sulfur content below 0.03 per cent is regularly obtained, and even lower if specifications require. The iron silicate slag required for the "shotting" operation and for incorporation in the matrix of iron is melted in two basic-lined, oil-fired tilting open-hearth furnaces. The molten slag is teemed in the batches required from time to time for the make-up needs of the operation.

Pouring, or "shotting," described in greater detail in the papers previously referred to, is the key operation. Refined iron from the

converter is poured in a steady stream into a vessel of slag directly below the metal ladle. The latter automatically oscillates and moves forward and backward, insuring uniform distribution of metal into the slag.

With ample volume of slag at a temperature maintained well below the freezing point of the refined metal, continuous solidification of the metal takes place; and accompanying this is the liberation of all of its dissolved gases with sufficient force to disintegrate the metal and produce a spongy ball of iron, impregnated with the liquid slag.

The general size of bloom in today's practice is three to four tons, and the pouring rate is one ton per minute. The "shotting" cups are on



FIG. 2.—THE OPEN-HEARTH FURNACE TILTS THE SILICEOUS SLAG INTO A LADLE.

cars, so that the decanting of surplus slag and the dumping of the sponge ball is effected at a station remote from the pouring platform. Pressing and rolling follow on the original heat of the ball, to intermediate products of billets or slabs conforming to standard mill practice. Furnaces, mills, and auxiliary equipment, as well as man power, conform closely to the standards of the modern rolling mill. The present output of the plant is more than 800 tons per day. Most of the product, skelp, plate, etc., is rolled from solid sections, in marked contrast to older wrought-iron practice of building muck bar piles.

Figs. 1, 2, 3, 4 and 5 illustrate the several phases of the processes, from the refining of the metal in the converter to the dumping of the sponge ball before pressing to a bloom and rolling.

From the viewpoint of wrought-iron manufacture, the new process measures up to the specifications set:

1. It will produce a material conforming to quality characteristics.
2. Aggregate output or unit size of bloom is entirely a matter of engineering expediency and judgment.
3. Manufacturing possibilities are present that should attract the marginal and diversified markets.

In addition, there is the added advantage that the flexibility in and control of the integral steps of the process lend themselves to improvement of quality of product or to meeting special service requirements.

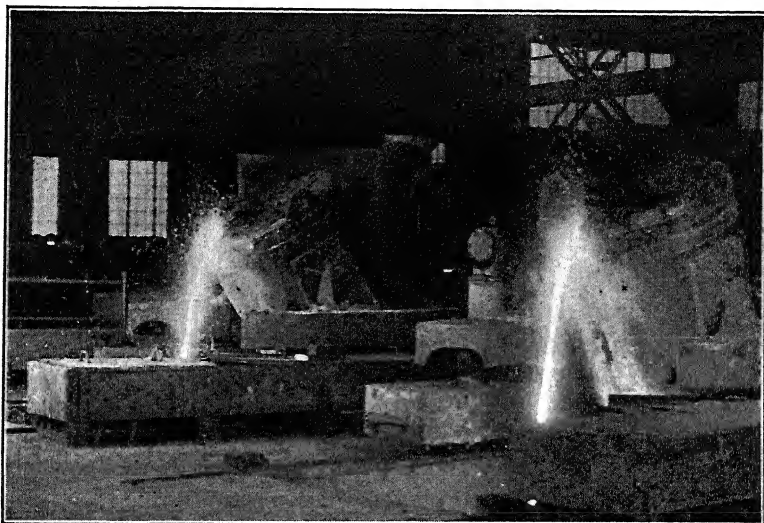


FIG. 3.—THE KEY OPERATION—PROCESSING OF REFINED METAL AND SILICEOUS SLAG.

QUALITY CHARACTERISTICS OF WROUGHT IRON

In the past, wrought iron had the puddling process for its background; and the process clause was an integral part of most specifications. Obvious disadvantages, such as failure to recognize the varying methods of the past or the changing trend of the present and the possibilities of the future, led the American Society for Testing Materials, in 1930, to depart from the plan of designating the permissible method of manufacture and to define wrought iron as a characteristic material, as follows:

Wrought iron is a ferrous material, aggregated from a solidifying mass of pasty particles of highly refined metallic iron, with which, and without subsequent fusion, is incorporated a minutely and uniformly distributed quantity of slag.

Material made in accordance with this specification, or having the characteristics resulting from such procedure, will be wrought iron of quality. It excludes steel, no matter how low in metalloids; also adulter-

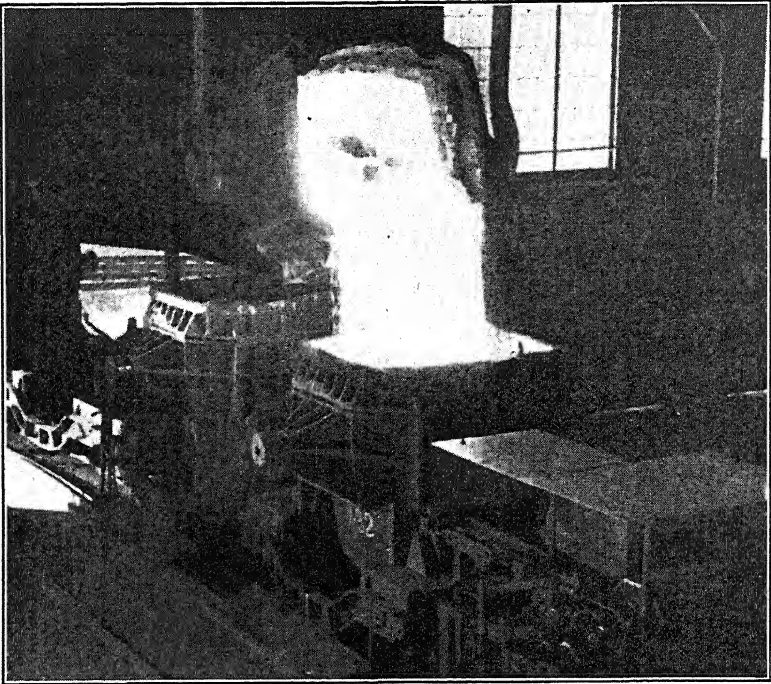


FIG. 4.—SURPLUS SLAG IS POURED FROM LADLE, LEAVING WHITE SPONGE OF WROUGHT IRON.

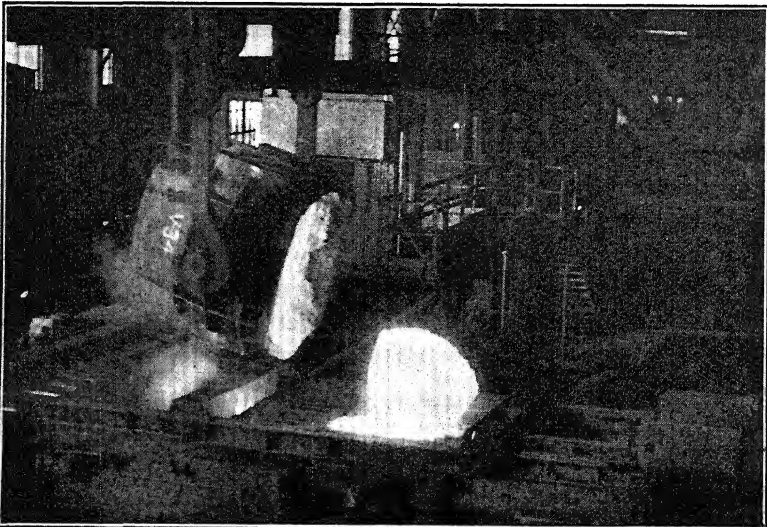


FIG. 5.—SPONGE BALL IS DUMPED ON PLATFORM OF 900-TON ELECTRICALLY DRIVEN PRESS.

ated material resulting from busheling. However, it is a technical definition, which involves features of refinement of base metal and character of slag distribution that may be set only by experience and comparison.

It soon became apparent that it was more than ever imperative that there should be an authoritative guide setting forth the standards of quality for wrought iron. One has been published by that society and, as an active worker on the committee that compiled the report, the writer will use it as the basis of this section. The reader is referred to the document in question for greater elaboration than the scope of this paper will warrant¹.

The consideration of quality in wrought iron resolves itself into two major divisions: (1) the detection of mongrel material containing steel scrap added in busheling or piling and (2) the determination of the finer points of quality in a product made by processes of recognized merit. Methods to be applied are in most respects common to both phases, and are related to the physical properties, chemical composition, and internal structural characteristics of the materials.

PHYSICAL PROPERTIES

The physical properties of wrought iron are essentially those of pure iron modified, only slightly in general practice by metalloid content of the base metal, and profoundly by the quantity and distribution of the incorporated slag. Up to certain limits, ductility is increased by greater work in forge or mill, due to finer and more threadlike distribution of the slag. This is reflected in the common practice of the puddle mill of once or twice piling in products designated as "single" or "double refined." Obviously, a similar result will be achieved by rolling relatively large initial blooms into small final sections.

In comparison with steel or ingot iron, the longitudinal ductility of wrought iron is somewhat lowered by the slag incorporation, while the transverse strength and ductility are markedly affected. However, rolling history is an important factor with respect to quantity and direction of reduction.

Physical properties are the engineer's guide in the design of structures, and thus are as important in wrought iron as in other metals. To the extent that steel adulteration affects the physical properties, or that variation in the inherent quality of wrought iron is reflected in this feature, such methods of testing have value. Broadly speaking, however, the usual physical properties of wrought iron are of minor significance

¹ Quality Standards for Wrought Iron. *Proc. Amer. Soc. for Test. Mat.* (1934) 34, pt. J.

in the detection of adulteration or in the determination of the finer points of quality.

CHEMICAL ANALYSIS

Chemical analysis has a place in the determination of wrought-iron quality comparable with its importance in the steel industry. One must bear in mind, however, that the customary metalloids may be in greater or less degree alloyed with the base metal or associated as oxidized constituents with the intermingled slag. The commonly reported analysis of wrought iron lists the carbon, silicon, sulfur, phosphorus and manganese of the composite; the ideal determination should separate the metal from the slag, and note the metalloid distribution between the two. Separation of slag from metal is quantitatively feasible, and progress is being made on methods for determining distribution of the several elements. As yet the latter are not adapted to general laboratory procedure. A few comments will serve to emphasize the significance of the several metalloids:

Carbon.—A high degree of refining without after additions results in low carbon content in wrought iron. It is quite typical to have 0.02 to 0.03 per cent, yet in some cases, 0.08 to 0.10 is retained by preference. Higher amounts arouse suspicion of adulteration by steel scrap or poor refining practice.

Silicon.—Normally this element is almost entirely a constituent of the slag, the usual amount of silicon being 0.10 to 0.20 per cent. Slag quantity and degree of silication cause certain variations, according to manufacturer's preference or nature of product. Repeated working tends to reduce the amount as reflected in the analysis report.

Sulfur.—This element is always undesirable. In well made wrought iron it should be under 0.05 per cent, and 0.03 or under is quite common. Lower sulfur is attained by special precautions and for special requirements.

Phosphorus.—This metalloid is almost invariably higher in wrought iron than in steel. It must be borne in mind that it is in part alloyed with the base metal, and in part associated with the slag. Good wrought iron may have 0.10 per cent or less, to 0.25 per cent or more, according to manufacturer's preference, nature of raw materials, or adaptability to service conditions. The lower order is advisable for materials subjected to shock, high temperature, or requiring higher ductility.

Manganese.—This element is usually under 0.05 per cent, owing to refining conditions and no after additions. This characteristic has caused a manganese content of 0.10 per cent or more to be taken as indicative of steel-scrap adulteration. Low manganese in wrought iron has usually been an earmark of quality; although there is no logical

ground for condemning an otherwise well made product because of a relatively high manganese content.

STRUCTURAL CHARACTERISTICS

In view of the composite nature of wrought iron, its quality is obviously affected by the nature of the association of base metal and slag. Methods of disclosing this internal structure have an importance greater even than the prominent place in the steel industry assigned to them by the metallurgist.

Wrought iron exhibits a well recognized fibrous fracture, in marked contrast to the crystallinity of steel. The nick bend, or fracture test, has long been a favorite way of rapidly distinguishing wrought iron from steel. Confusion may result at times, because of a semblance of fiber in dirty steel or a pseudocrystalline break in wrought iron due to high carbon, high phosphorus, overheating, or sudden fracture. The fracture test has a doubtful and, at best, a secondary value in detecting scrap adulteration in the product.

Macroscopic etching will reveal methods of piling, and adulteration where the addition of steel scrap is sufficient in quantity or has a coarseness of distribution to permit the naked eye to distinguish between the woody etch of wrought iron and the comparatively smooth surface of steel. Deep etching has a useful place, but is of no great assistance in the determination of the finer points of quality.

It is to the metallographic microscope that the wrought-iron metallurgist is most deeply indebted. It has given us our present-day understanding of wrought iron, and may be considered as the court of last resort in quality determination. The structure of wrought iron is essentially a ferrite matrix, through which the slag is uniformly disseminated in the form of several hundred thousand filaments per square inch. Important disclosures of the microscope are:

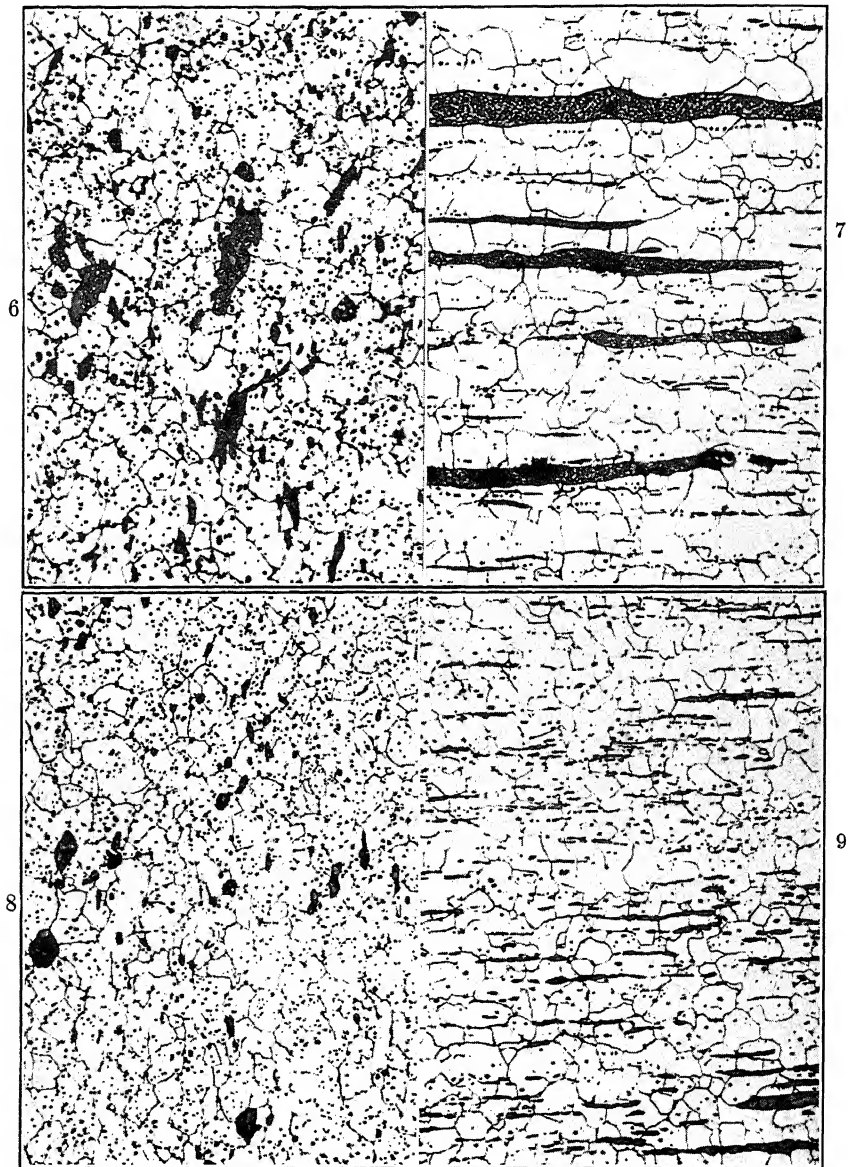
1. Grain size. Coarse grain, distortion, or lack of uniformity have a bearing upon quality in relation to mill history and use of product.

2. Pearlitic areas—the quantity and nature of carbon distribution, generally practically negligible or quite small in amount. Irregular or banded pearlite, coupled with an absence of slag is an evidence of steel adulteration.

3. Slag characteristics—type and distribution. Coarse, pocketed slag is undesirable. Finer textures result from progressive rolling reductions, and are promotive of better physical properties, especially ductility. As noted above, absence of slag in banded zones excites suspicion of steel adulteration.

4. Abnormalities—such as grain distortion, high-phosphorus ghost lines, and so forth.

The microscope is of no value in the detection of elements alloyed with the base metal in solid solution, such as manganese, silicon, copper, phosphorus, nickel.



FIGS 6-9.—EFFECT OF ROLLING REDUCTION. $\times 100$, REDUCED $\frac{1}{3}$ IN REPRODUCTION.

Light rolling: Fig. 6, transverse; Fig. 7, longitudinal.

Heavy rolling: Fig. 8, transverse; Fig. 9, longitudinal.

Finer grain size and slag texture of heavy rolling reduction is noted in contrast to coarser distribution with less reduction in section.

Anatomical characteristics of wrought iron are of greatest significance from a quality viewpoint. Judgment should be based upon ample experience, and be fully cognizant of the objective, so that criticism of material is not based upon isolated or irrelevant imperfections, but upon their prevalence and whether or not they typify the character of product and are of influence upon the quality and particular service requirements of the material.

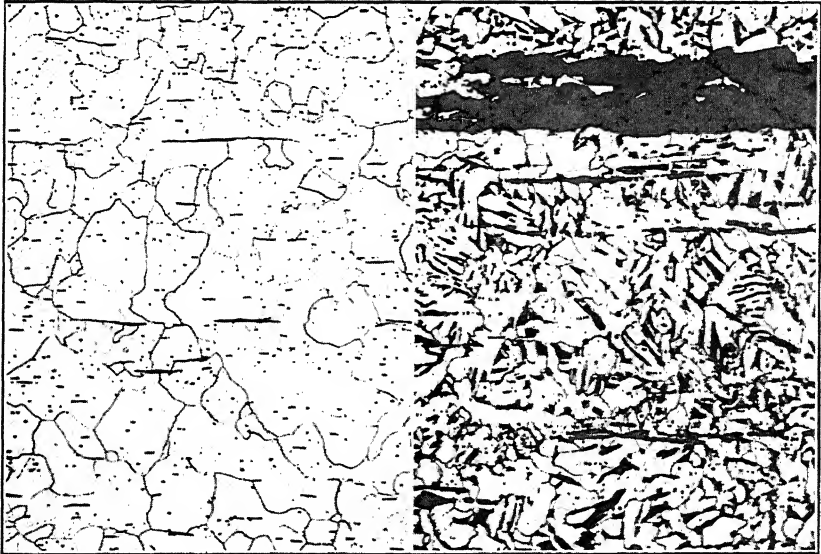


FIG. 10.—ABNORMALITIES, DEFICIENCY IN SLAG. LONGITUDINAL. $\times 100$, REDUCED $\frac{1}{3}$ IN REPRODUCTION.

Effects of rolling and finishing temperatures are indicated in grain size. There is an almost complete absence of slag, and material is abnormal in this respect. It is not necessarily defective unless this deficiency is typical of the entire section.

FIG. 11.—ABNORMALITIES, PEARLITE (CARBON) AREAS, RESULTS OF INCOMPLETE REFINING, LONGITUDINAL. $\times 100$, REDUCED $\frac{1}{3}$ IN REPRODUCTION.

Photomicrograph shows carbon in spotty distribution. Presence of slag in carbon areas indicates that product has not been result of scrap adulteration. Material can be criticized but its condemnation should rest upon thorough exploration of entire section to determine extent of abnormality illustrated.

A few photomicrographs (Figs. 6 to 13) are appended to illustrate typical structures and features related to the quality characteristics of wrought iron.

Wrought-iron quality has reasonably definite metallurgical standards. Provided these are met, the process of manufacture is of no particular importance. In fact, there is no metallurgical means by which the process of manufacture may be detected, provided the product is wrought iron conforming to the quality standards recognized and set forth somewhat briefly in this discussion.

ADAPTABILITY OF WROUGHT IRON

In the past few decades, the sustaining factors back of the wrought-iron industry have been a substantial recognition of its merit against corrosion influences and to withstand shock and fatigue stresses. In spite of manufacturing limitations of the past, the industry has held to a substantial level. It is a mark of commendation that wrought iron has in the past filled the varying needs with a single-characteristic mate-

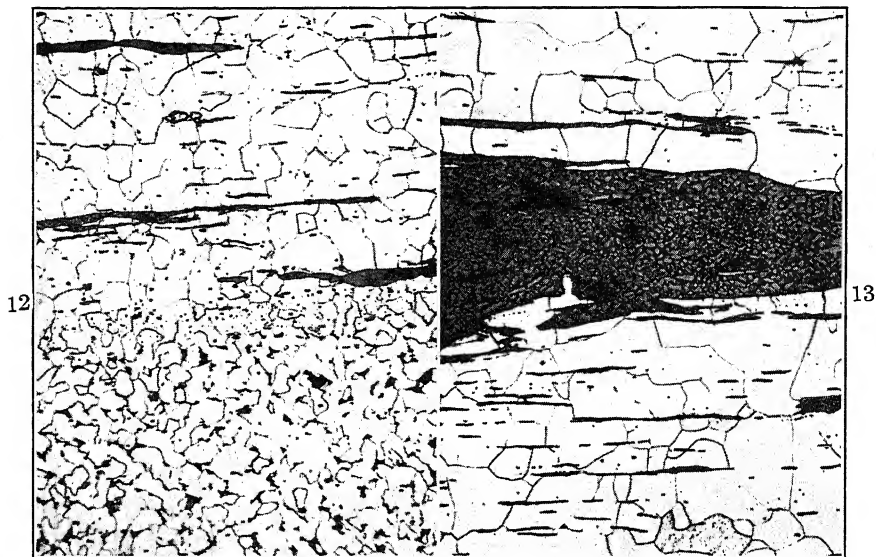


FIG. 12.—ABNORMALITIES, PEARLITE (CARBON) AREAS, RESULT OF STEEL-SCRAP ADULTERATION, LONGITUDINAL. $\times 100$, REDUCED $\frac{1}{3}$ IN REPRODUCTION.

Banded nature of carbon-bearing zones, with absence of slag in these zones, and relatively good wrought-iron structure shown in adjoining bands, is indicative of scrap adulteration in busheling or piling.

FIG. 13.—ABNORMALITIES, LARGE SLAG AREAS, LONGITUDINAL. $\times 100$, REDUCED $\frac{1}{3}$ IN REPRODUCTION.

Coarse slag areas are likely to result in poor ductility and strength, in faulty machining quality, and in liability to tear in bending or other forming operations.

rial and with the minimum of flexibility and technical control which has been in the past associated with the methods of manufacture. Wrought iron of the future will not and cannot afford to depart from those quality characteristics that have made its background; but there is reason to expect that it will improve upon these to the extent that advanced state of knowledge and new methods of manufacture may make possible.

Transition in manufacturing methods has extended the horizon of possibilities as compared with past orthodox practices. Greater control during manufacture, as affecting the nature of the base metal and the slag, and particularly the distribution of this intermingled slag, has

enhanced the serviceability of wrought iron by bringing all of the product to a uniformly high standard of quality.

Proper adjustment of slag character has resulted in marked improvement in welding in pipe manufacture; while control of the distribution of the intermingled slag has made it possible to produce pipe that will meet requirements for close radii in bending and coiling which formerly were accompanied by excessive losses due to tearing.

The necessities of transverse bending, during flanging or similar forming of plate prompted a study of rolling practice, with the result that by suitable modification it is now feasible to produce plates with equal properties in the major directions. The resultant ductility is approximately one-half of the summation of the usual longitudinal and transverse values. Plate-forming operations are now regular practice, which formerly were accompanied by great risk and high loss, or in many cases were impossible. The American Society for Testing Materials has modified its plate specification to recognize this fabrication need.

In the puddling operation, alloy base metals were possible only to the extent that the additions could be made in the preliminary stages of melt-down, and would remain unaffected by the strong oxidizing influences in refining. Additions could not be made on completion of the heat. In the Byers new process previously alluded to, the range is much extended; being limited only to the extent that the alloy addition may be controlled and that it does not seriously affect the plastic welding qualities of the sponge ball. The field of alloy wrought iron is largely unexplored, but is worthy of study, since improvement in strength and special properties to meet physical requirements of service will be obtained, without loss of the other desirable features inherent in wrought iron. Nickel and copper have proved useful in this respect; the former, in particular, has improved the strength and elastic properties. Nickel wrought iron has given exceptional performance in oil-well sucker rods, where the service condition of corrosion-fatigue is a serious problem.

Wrought iron is a quality product, and as such it must be fitted to its special fields of application on the basis of service rendered per dollar of cost. Today's trend is to combine different materials within the same structure toward accomplishment of greatest ultimate life and balanced design. The wrought-iron technologist can be a valuable aid in this direction, in analyzing the need and in placing his product in its qualified channels. In later years manufacturing limitations have caused wrought iron to find its outlet in the form of welded pipe and bar-iron products. The major conditions of corrosion and fatigue are equally important in the service requirements of other commodities. Better manufacturing facilities have made possible the reintroduction of plates, sheets and other products that have not been available for a few decades. Already substantial progress has been made in the manufacture and distribution of

flat rolled products to users in railroad, government, utilities, industrial, oil and marine fields.

The removal of manufacturing handicaps should expand the outlets for wrought iron into marginal fields of application; this will involve an economic study considering both serviceability and installed cost in relation to other competing materials.

The major manufacturing companies have adhered to quality standards in their products, and have done much by educational efforts to remove ignorance and misconception on the part of the user. In particular, they have directed attention to the subterfuge, in some fields, of supplying a request for quality wrought iron with a product made by busheling common scrap. Such practice has harmfully affected the industry as a whole, since the unsuspecting user has vented his dissatisfaction when failure occurred upon wrought iron and the wrought-iron industry, including therein the conscientious as well as the unscrupulous producer.

The misconceptions regarding wrought iron on the part of users are amazing. For the common good the haze must be lifted by advertising of an educational character, and by subordination of points of more or less hypothetical importance which tend to confuse the issue.

It is no indictment of an industry to accuse it of leaning upon its past. If the past has been commendable, and particularly where, as for corrosion conditions, a life history usually of long duration is necessary to determine the merit of a material, service records form the only reliable means of evaluation. It is unfortunate that for many of the conditions for which wrought iron has a place quick time tests of selection or evaluation have not been developed to the point of reliance upon their results.

The wrought-iron industry is taking advantage of all the features that have been associated with the best hand-puddling practice; but rather than holding them as the bull's-eye of the target of achievement, it is making them serve as a foundation for greater progress in the future. Tradition will be a diminishing factor, except where it squares with experience and factual service records.

The future has been made easier through passing the difficult hurdle of manufacture. Traditional quality must and will be maintained. The industry will rest upon this background; but its future will be linked up with diversification of products and specialization of type to fit special needs.

DISCUSSION

(Francis L. Toy presiding)

T. T. READ,* New York, N.Y.—Has this new development led to what I might describe as a considerable reorganization of the uses of wrought iron?

* Vinton Professor of Mining Engineering, School of Mines, Columbia University.

J. ASTON.—As you know, wrought iron has gradually, through the years, come to limited outlets for products that would best lend themselves to production and would also be the best channels for realizing the service qualities of wrought iron. The result has been that in more recent years the markets have been primarily those for pipe products and bar iron, particularly bar iron intended for fatigue service; whereas formerly wrought iron was used for almost all commodities and had considerable markets in plate, in sheet materials, and wire. In recent years the latter outlet has largely faded away.

We are now rolling plate in limited amounts; also sheet bar, which is being converted to sheets in outside mills. We have made wire, but this is only in the experimental stage. We are furnishing raw material to certain of the bar-iron manufacturers, and the horizon in this respect is being broadened. Then there is a possible expansion, as I have pointed out, which is in fact now an actuality to a limited degree, in material of higher strengths than the usual normal wrought iron.

In this field, nickel wrought iron is giving good service because of its ability to withstand corrosion fatigue.

MEMBER.—I cannot imagine anyone making a suggestion that would improve on your operation, but what is to stop you from forming slag in a cupola?

J. ASTON.—When we were doing our experimental work, we used a cupola and it worked very satisfactorily. At the Warren operation, which has been described, at first we had cupolas for that purpose. So long as we were running experimentally for a duration of, say, an hour, it would melt beautifully, but when we got into continuous melting, which was, of course, necessary, we found that salamanders formed in the hearth of the cupola because of a blast-furnace action of reduction of the iron oxide. In the emergency we turned to the reverberatory furnace and have held to this method since.

Alluding to Mr. Ramseyer's suggestion of pouring molten pig iron through a granulated medium to refine and decarbonize it to continuously produce steel, there is a parallelism to what we are doing, which points to a difficulty in his path. With the rise of fusion point of the metal as decarbonization takes place, formation of a sponge ball such as we produce will occur, unless he can find a medium of proper oxidizing power which will remain solid and granulated while being heated to temperatures higher than 2700° F.

The "Plasticity" of Iron at Low Temperatures

BY K. HEINDLHOFER,* KEARNY, N. J.

(New York Meeting, February, 1935)

ESTIMATES of the "plasticity" of a metal are commonly deduced from three types of test—tensile, torsion and impact. The several results have been more or less at variance, though this disparity has attracted little notice, largely perhaps because they have been expressed in different terms. The discrepancy between the results of the three tests becomes obvious when each is made at a series of low temperatures, for the temperature range within which the "plasticity" of iron largely disappears proves to be very different in the three types of test. The rather abrupt disappearance of "plasticity" of iron within a narrow temperature range cannot be due to any physicochemical change (such as a precipitation) taking place in the material at that time, because the original plasticity is immediately regained when the temperature of the material is brought above the sensitive range. Accordingly this difference in behavior shows that the "plasticity" of a metal depends upon the mode of action of the stresses which produce the deformation, and therefore upon the method of test.

Analysis of the stresses leads to the conclusion that the observed plasticity of a metal is determined by the relation between its resistance to rupture by separation and its resistance to shear (slip), on the one hand, and between the effective normal and shearing stresses on the other; and that the relation between the two resistances does not in general remain constant with change of temperature, and may somehow be altered to some extent by the previous treatment of the specimen. This suggests the view that the results of none of the usual mechanical tests are directly comparable even for a single metal tested at a series of temperatures, or for a series of metals at one temperature, because the proportion of the total resistance of the metal to the test contributed by the

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* Research Laboratory, United States Steel Corporation.

resistance to rupture (cohesive strength) and the resistance to shear respectively would not in general be constant.

Before proceeding to discuss the difference in the incidence of the stresses set up in the specimen in the three main methods of test, let us examine the data available from comparable tests made at a series of temperatures. Typical results are presented in Fig. 1.

Notched-bar Impact Test.—Mailänder,¹ working with bars of a tough low-carbon steel broken on an impact machine, showed a rapid fall in impact strength with decrease in temperature. This phenomenon has been noted by others, including B. M. Larsen (unpublished data from this laboratory) who, testing $\frac{1}{4}$ -in. dia. cylindrical specimens with a circular V-notch on a Charpy machine, found a similar rapid decrease on a variety of low-carbon steels as well as on iron carefully purified in hydrogen to a point at which it contained extremely small quantities of nonmetallic elements; and established the fact that the specimens regain immediately their original ductility when again warmed above the sensitive range. The temperature impact curve for this purified iron is shown in Fig. 1. It should be noted here that the location of this "susceptible range" varies, depending not only upon the previous treatment of the specimen but also upon the sharpness of the notch, which governs the relation of normal to shearing stress at the bottom of the notch.

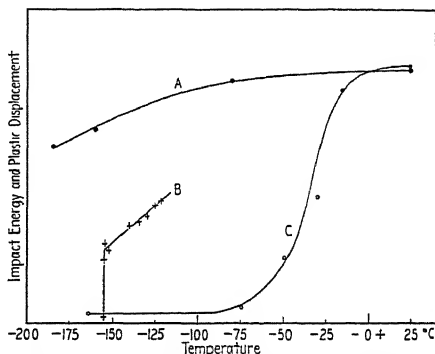


FIG. 1.—INFLUENCE OF LOW TEMPERATURE ON (A) ANGULAR DISPLACEMENT IN TORSION, (B) ELONGATION IN TENSION, (C) ENERGY ABSORBED IN IMPACT; INDICATING DISAPPEARANCE OF PLASTICITY AT DIFFERENT TEMPERATURES IN THE SEVERAL TEST METHODS.

Tensile Test.—Observations dating back to 1871 indicate the apparent embrittling effect of low temperature upon steel tested in tension.² The liquefaction of air made available a temperature range down to about -185° C. and Hadfield³ made in Dewar's laboratory a large number of tensile tests on various steels and other metals at these low temperatures. He reported that the elongation of commercially pure iron (such as

¹ P. Goerens and R. Mailänder: Prüfung und Untersuchung der Metalle und Legierungen, 305, Fig. 102. Wien-Harms Handbuch der Experimental-Physik. Akad. Verlagsgesell., Leipzig, 1930.

² D. Forbes: Quarterly Report on Progress of the Iron and Steel Industries in Foreign Countries. *Jnl. Iron and Steel Inst.* (1871) 2, 371.

³ R. A. Hadfield: Experiments Relating to the Effect on Mechanical and Other Properties of Iron and its Alloys Produced by Liquid Air Temperatures. *Jnl. Iron and Steel Inst.* (1905) 67, 147-255.

Swedish charcoal iron) has dropped from 25 per cent at ordinary temperature to practically zero at -185° , but did not determine the temperature range within which this drop occurs. He also observed that the phenomenon is reversible in the sense that the usual elongation is regained when the material is again brought up to room temperature.

Recently de Haas and Hadfield⁴ extended the range down to the boiling point of liquid hydrogen (-253° C.), testing 41 metals and alloys. Of these only six remained plastic at -253° C.; namely, two high-percentage nickel steels, a nickel-manganese alloy, the 18-chromium 8-nickel stainless steel, and the elements nickel and copper. It is noteworthy that the elongation of copper in the tensile test increases with decreasing temperature, reaching 60 per cent at -253° C.

Sauerwald and Schmidt⁵ have shown recently that the change in elongation in tensile test on low-carbon steel is not gradual, but rather abrupt about -155° C. The brittle fracture goes generally through the grains, only occasionally through grain boundaries.

Torsion Test.—The present writer applied a torsion test to cold-rolled bars $1\frac{3}{64}$ -in. dia., 1 in. long, of pure iron at several low temperatures down to liquid-air temperature, and found that they could be twisted through a surprisingly large angle, about four complete revolutions, before rupture by shear occurred. Hence the range in which plasticity of iron in torsion disappears lies below liquid-air temperature.

Altogether therefore there is a rather abrupt change in the apparent plasticity of a low-carbon steel or of iron, which in normalized pure iron occurs at a temperature of -20° to -30° C. for the impact test as made, but not until -155° C. for the tensile test, and is below -185° C. (if indeed it occurs at all) for the torsion test. The precise temperature range undoubtedly varies to some extent with the material and with its previous treatment, and with the precise shape and size of the specimen, but the differences in temperature between the three types of test are so great as to be inescapable.

The abrupt change in apparent plasticity might be thought to be due to some physicochemical change in the metal, such as precipitation of some phase from solid solution or possibly even the appearance of an allotropic phase. But the hypothesis of precipitation is untenable because the process of re-solution of the precipitated phase could not possibly go on rapidly enough at these temperatures to enable the material to regain its original plasticity as soon as it is warmed above the apparent

⁴ W. J. De Haas and R. A. Hadfield: The Effect of the Temperature of Liquid Hydrogen (-252.8° C.) on the Tensile Properties of Metals. *Phil. Trans. Roy. Soc.* (1933) **A715**, 231; abridged in *Engineering* (1934) **87**, 331-333.

⁵ F. Sauerwald, B. Schmidt and G. Krämer: Über den Sprödigkeitsbereich von Eisen bei tiefen Temperaturen. *Ztsch. Physik* (1931) **67**, 179-183.

brittle range. No allotropic change in iron below 0° C. has ever been observed; and even if there were one, it is quite unlikely that its speed would be great enough to permit of the rapid reversibility of the phenomenon as observed. Moreover, we would have to assume the occurrence of at least two such changes—one for the impact, one for the tensile test—and predicate further that the change affecting the impact test is without influence in the tensile test in that temperature range. We are therefore constrained to turn from any explanation that involves a rapid change in the structure of the metal towards factors that may differ from one type of test to another, the most obvious differences being the different character of the stress applied in the several tests.

NATURE OF STRESS IN SEVERAL TESTS

Let us consider first the simplest case, the tensile test, a schematic representation of which is depicted in Fig. 2a. AA represents the specimen, O is an arbitrarily chosen point on the axis of the specimen and BB is an arbitrary plane through the point O ; FF represents the applied external force. We can imagine the specimen separated into two parts along BB , and consider either part separately (Fig. 2b). Static equilibrium requires that the downward pull on the upper part is precisely equal and opposite in direction to the upper external force F . It is convenient to resolve F at the point O into two components (Fig. 2c), one (N) perpendicular to and the other (S) within the plane BB . The corresponding normal stress n and shearing stress s are obviously N/a and S/a respectively, a being the area of the section BB .

The effect of these two types of stress acting upon the solid is quite different. The normal stress, if sufficiently intense to overcome the cohesive strength of the material, disrupts the specimen on a surface perpendicular to the direction of the stress. The shearing stress, on the other hand, as soon as it exceeds a certain limit, causes gliding or slip within the specimen in the plane along which this stress is a maximum. It is thus evident that the specimen may rupture without appreciable deformation if either the inherent cohesive strength of the material is small or the normal stress is large; and that plastic deformation will occur readily if either the inherent resistance to shear is small or the shearing stress is large. Consequently the character of the failure or deformation of a stressed solid body depends upon the relative magnitude not only of its own inherent resistance to rupture and to shear but also of the maximum normal stress to the maximum shearing stress acting upon it.

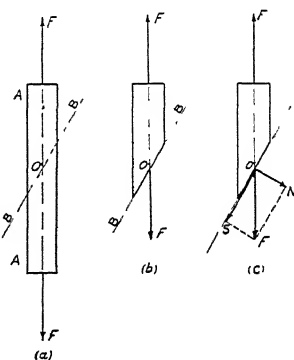


FIG. 2.—RESOLUTION OF TRACTION INTO A NORMAL AND A SHEAR COMPONENT.

Moreover, the differing behavior of different materials indicates that resistance to rupture may be large while resistance to shear is small, and conversely, and that the temperature coefficient of these two quantities may differ markedly.

In the tensile test, the greatest normal stress acts on a plane perpendicular to the axis of the specimen; the greatest shearing stress is set up in a plane inclined at 45° to the axis; and the greatest normal or rupture stress turns out to be twice the greatest shearing stress. From this it follows that if the strength properties of the material are such that its resistance to rupture is less than twice its resistance to shear, a tensile-test specimen will break in a brittle manner without deformation, regardless of its absolute plasticity, for under these circumstances this quantity plays no role.

A similar stress analysis of the simple torsion test shows that in this case the maximum normal stress is equal to the maximum shearing stress. Obviously, therefore, for a given material and a given resistance to normal stress, a greater shearing stress can be developed in the torsion than in the tensile test before failure occurs; in other words, gliding or plastic deformation of the material in torsion can continue to occur without rupture when in the tensile test the limit of cohesion would already have been reached. Thus a tensile test will indicate brittleness and a torsion test plasticity in any material of which the resistance to shear is between 50 and 100 per cent of its resistance to rupture.

In the notched-bar impact test, a moving mass, usually a pendulum, strikes either the end or the middle of a bar-shaped specimen and the loss of kinetic energy of the moving mass is observed. This energy absorbed in deforming the specimen is taken as a measure of impact strength, or of the "plasticity" of the material, under the specific conditions of the test. A material that absorbs little kinetic energy breaks without appreciable deformation—that is, fractures in a brittle manner—for the amount of energy absorbed is the product of the displacement and the resistance to deformation. Conversely, a large energy absorption implies a plastic material, where considerable deformation precedes fracture. A precise stress analysis of this test is difficult, and is complicated by the impact character of the load, though there is reason to believe that for ordinary speeds of impact this complication is not significant. Recently Neuber⁶ has given a mathematical solution of the stress distribution in a notched bar in tension, from which it may be reasonably inferred that in the case of a notched bar in bending the maximum normal stress is still greater in comparison with the maximum shearing stress than in the ordinary tensile test.

⁶ H. Neuber: Elastisch-strenge Lösungen zur Kerbwirkung bei Scheiben und Umdrehungskörpern, *Ztsch. f. ange. Math. u. Mech.* (1933) **13**, 439–442.

Thus for a given shearing stress in the material, the normal stress is greatest in the impact, intermediate in the tensile, and lowest in the torsion test. This order of the tests is the same with respect to the temperature at which brittleness sets in, being highest (about -30° C.) for the impact, about -155° for the tensile, and below -185° C. for the torsion test. Now, rupture without plastic deformation—that is, a brittle fracture—occurs at the temperature at which the cohesive strength is just exceeded by the prevailing normal stress while the resistance to shear still withstands the prevailing shearing stress. It seems not unreasonable therefore to ascribe this difference in “plasticity” to the different combination of normal and shearing stress in the several test methods, and to a change with temperature in the relation between the resistance to shear and the resistance to rupture. The former is known to increase as the temperature is lowered; the latter presumably also increases, but no direct determination has yet been possible. The most reasonable hypothesis, which accounts completely for the phenomena observed, is that the inherent resistance to shear increases more rapidly with falling temperature than does the inherent resistance to rupture. This hypothesis implies directly that when we make the same test on a material at different temperatures, we are testing a different combination of its inherent properties, and therefore that the results of such mechanical tests may not be strictly comparable even for a single material. However this may be, it is obvious that any conclusions we may draw as to the plasticity or brittleness of a material under given conditions must depend largely upon the test method used as a criterion.

All of this serves to emphasize the importance of the fact that the state of stress in a solid body, even if it is isotropic and homogeneous, is not defined by a single quantity—such as a certain number of pounds per square inch—which suffices in the case of gases or liquids. It is defined completely only in terms of three, mutually perpendicular, so-called principal stresses; and the effect produced depends not only upon the absolute but also upon the relative magnitude of these three principal stresses. One limiting case may be mentioned; namely, that the three principal stresses are all equal and directed outwards. This can be imagined as a solid sphere with innumerable wires attached to its surface, all in equal radial tension. When the tension exerted by the wires becomes sufficiently large, the sphere will rupture without any deformation even though it were of a material of high inherent plasticity such as lead, by reason of the absence of shearing stress. This example is difficult to realize, though it may occur in the interior of larger masses of steel that have been cooled too rapidly through the critical zone; it is significant because it represents the ideal conditions requisite to a determination of the true cohesive strength of a solid. The cohesive strength thus determined would be more nearly a real physical property of the

material than is the ultimate tensile strength deduced from the ordinary tensile test, which is a complex quantity influenced by plastic flow (cold work) preceding the fracture and by the resultant change in shape and dimensions of the specimen. It would lead too far to go into this important question now; but attention may be called to a recent valuable paper on cohesive strength by Kuntze⁷ who, from a systematic investigation of the tensile test applied to specimens with circular notches of different depth and angle, reaches the conclusion that in this way a better estimate of the real cohesive strength can be derived than by the conventional methods.

Similar reasoning applies to other cases of apparently contradictory plastic behavior of materials; for instance, to "temper brittleness," that is, notched-bar brittleness observed in certain quench-hardened chromium-nickel and other steels after slow cooling from a drawing temperature of about 400° C. In the tensile test they elongate to the extent that can be expected as usual after such a heat treatment, but in the impact test their apparent plasticity is disappointingly low. This led W. H. Hatfield⁸ to propose a distinction between true plasticity as measured by relative elongation or reduction of area, and the notched-bar plasticity or its inverse, the notched-bar brittleness. Here again neither test leads to a true plasticity; this is approached most nearly in the torsion test. But even there the shearing stress cannot be produced alone except in the cross-section normal to the longitudinal axis of the specimen; in all other sections the shear is accompanied by either tensile or compressive stresses, which may influence the observed result.

SUMMARY

The fact that the temperature range within which the "plasticity" of iron diminishes abruptly differs markedly with the type of test—notched-bar impact, tensile, torsion—led to the viewpoint outlined in the preceding pages; which points out that the indications of these tests cannot be identical because the relative values of the three principal stresses acting upon the specimen are entirely different in these three types of test. The phenomena indicate that, as the temperature falls, at least below ordinary temperature, the true cohesive strength of the material increases more slowly than does its shearing strength, in other words, that the relation between these two quantities changes. This suggests that a mechanical test of different materials, or even of the same material at different temperatures, does not necessarily yield comparable deductions as to the inherent properties of the material.

⁷ W. Kuntze: Kohäsionsfestigkeit. Berlin, 1932, Julius Springer.

⁸ W. H. Hatfield: The Mechanical Properties of Steels. *Engineering* (1919) 107, 615-619.

Gases in Metals

By C. A. EDWARDS*

(Institute of Metals Division Lecture†)

ABSTRACT

FOLLOWING a brief introduction, an outline is given of the four main conditions in which gases may be associated with metals; namely, (1) adsorbed gases, (2) dissolved gases, (3) gases in chemical combination, (4) gases entrapped in blowholes or cavities.

Adsorption is essentially a surface phenomenon and is regarded as the attachment of outside molecules or atoms to the exposed free valencies of the atoms comprising the surface layers. In many cases where adsorbed films of gas are formed this is accompanied by a process of diffusion of the gas into the metal itself. This is particularly true in respect to iron and hydrogen, and experiments have shown that there is no difference between the rate at which hydrogen diffuses through a single crystal of iron and through the same material after it has been recrystallized into a mass of small crystals. This does not prevent a somewhat greater concentration of gas at the boundaries of adjacent crystals, nor does it mean that the effect of the gas will be the same at the boundaries as it is within the body of the crystals. Indeed, under certain conditions, iron is rendered very brittle at the crystal boundaries, as shown in experiments by Pfeil with samples of almost pure iron.

Much work has been done by many investigators concerning the temperature and conditions under which dissolved hydrogen, in particular, can be at least partially removed from different metals. With iron, the hydrogen that has diffused into the metal as a result of acid attack by pickling or by electrolytic deposition of the gas on the metal is partly removed by exposing the metal to the atmosphere at ordinary temperatures. Considerably more can be eliminated by raising the temperature, and even greater quantities by jointly raising the temperature and reducing the pressure. Annealing at suitable temperatures completely removes the bad effects of excessive amounts of hydrogen dissolved in or associated with iron. This is shown by the data plotted in Fig. 1, giving values for electrolytic iron sheets after annealing at temperatures between 250° and 950° C. The hydrogen brittleness is rapidly diminished at

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about 250° C. and seems to be almost entirely removed after a short annealing at about 700° C. The change in properties is accompanied by a recrystallization of the metal similar to that which takes place during the annealing of heavily cold-rolled material.

When hydrogen diffuses into metals, it is apt to cause defects. When there are nonmetallic impurities in steel such as oxide of iron or slag

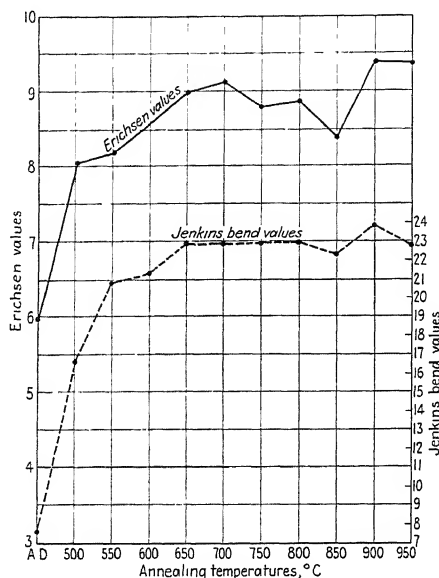


FIG. 1.—ERICHSEN AND JENKINS BEND VALUES OF ELECTROLYTICALLY DEPOSITED IRON SHEETS 32 MM. THICK.

inclusions, straightforward diffusion of the hydrogen is interfered with. Under these conditions, there is a distinct tendency for the hydrogen as it diffuses to the boundary walls of the inclusions to accumulate in the molecular condition and develop enormous internal pressures causing blisters.

In regard to the influence of temperature and pressure on the solubility of gases in metals, reference is made to the work of Sieverts, who found that the amount of gas capable of being held in solution by a given metal at a constant temperature was proportional to the square root of the pressure of a single gas. In the case of a mixed gas, the quantity of any one of them dissolved in the metal is proportional to the square root of its partial pressure.

The remainder of the paper deals with blowholes in castings and ingots of various metals, principally steel; more particularly in that class of steel known as "rimming steel." Details are given of experiments to determine the influence of varying amounts of oxygen and carbon upon the internal character of steel ingots, with special reference to the positions and general distribution of the blowholes in the ingots. Briefly, the

procedure was as follows: Sixteen pounds of commercial Armco iron rods was melted in a high-frequency furnace. After a specified temperature had been reached a definite amount of oxide of iron, corresponding to 0.195 per cent of oxygen, was added to each experimental melt and sufficient time allowed for this oxide to dissolve in the metal. The slag was then removed from the surface, the necessary carbon in the form of a synthetic iron-carbon alloy was added and then different quantities of

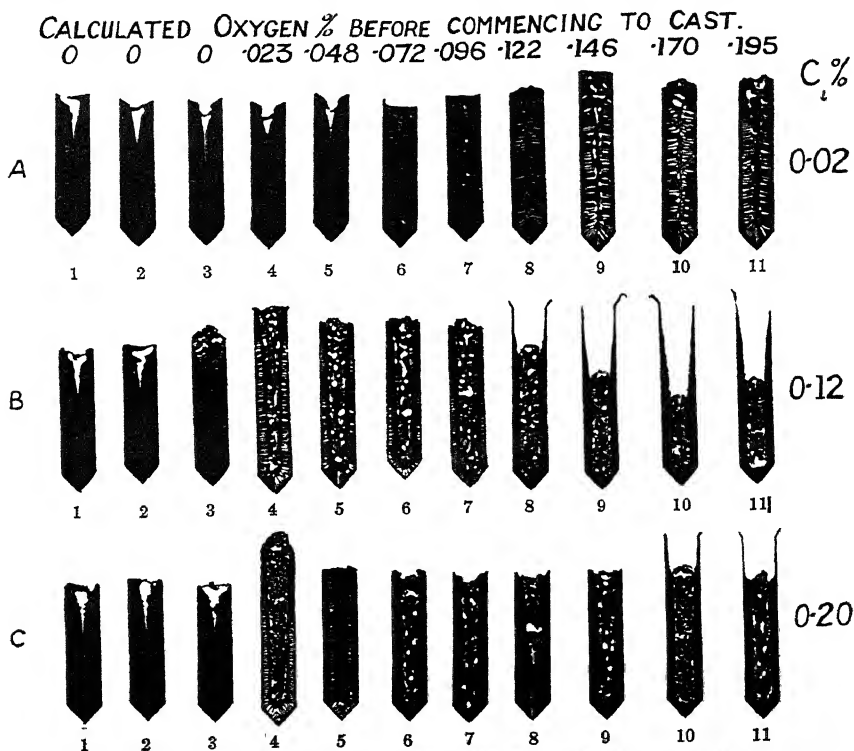


FIG. 3.—INGOTS CONTAINING VARYING AMOUNTS OF OXYGEN FOR CONSTANT CARBON.

metallic aluminum introduced to each melt belonging to a given series, and the metal cast at a constant temperature.

The results are shown in diagram form in Fig. 3, for the three series of ingots. Practically every type of ingot known in the steel industry is represented in these series. It is significant that only when the metal contains so much oxygen as to cause it to boil in the mold, or even in the crucible before casting, is a perfectly solid rim obtained. This implies that rimming is obtained only when so much oxygen is present as to cause vigorous boiling. It is believed that rimming is caused by chilling or supercooling effects disturbing the conditions of equilibria and causing abnormal segregation, thus forcing the reaction of oxide of iron and carbon to take place.

Steels for Die-casting Dies

By SAM TOUR,* MEMBER A.I.M.E.

(New York Meeting, October, 1934)

SOME years ago, the writer described heat checks or thermal cracks that occur in die-casting dies.¹ The life of dies was considered in relation to the casting temperature, the material used for the die, and the heat to be absorbed by the die per unit volume of casting made. The mechanism of the action that results in thermal failure of dies was described. In the present paper the writer proposes to describe some additional observations in regard to heat checking, make one or two suggestions as to the method or methods for further attack of the problem, and give the results obtained on some work carried out along these lines.

IMPORTANCE OF HEAT CHECKING

Heat checks in steel are the source of trouble in many industries besides that of die casting. Every shop where metals are subjected to hot working is searching for improvement and hoping for a cure. The development of a material of sufficient strength to be used as a die and yet devoid of the property of heat checking would be a godsend to many shops and many industries. The need for thorough study and research on the subject is evidenced by the wide variety of hot-working die steels on the market. It is peculiar, but true, that in practically every case the maker of the steel can give concrete evidence to prove his contention that his type of hot-working die steel is as good as or better than any other. A number of steel companies have several hot-working die steels from which choice can be made to fit a particular set of requirements. Possibly to expect one material to be universally the best hot-working die steel is unreasonable. In some hot-working operations, as in drop forging, the die must have great toughness to withstand the stresses developed; in other operations, as in hot piercing or punching, resistance to erosion at high temperatures, possibly defined as strength and hardness at elevated temperatures, is required. In still others, as in die casting, only sufficient hardness to resist scoring between moving surfaces is required, whereas the resistance to sudden changes in temperature must be at a maximum.

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* Vice President, Lucius Pitkin, Inc., New York, N. Y.

¹ S. Tour: Die Castings. *Jnl. Ind. & Eng. Chem.* (Jan., 1923).

FORMATION OF HEAT CHECKS

Heat checks, in the writer's opinion, are due to strains set up by repeated changes in temperature, and these strains, at some time or other, set up stresses that exceed the elastic limit or fatigue limit of the material in question. The amount of strain is a function of the difference in temperatures between two adjacent parts of the same block of steel; in other words, the temperature gradient. Assuming that the modulus of elasticity of steel is approximately independent of composition, the following properties should be sought for in the effort to obtain a steel with maximum resistance to heat checking: (1) minimum coefficient of expansion; (2) maximum thermal conductivity; (3) maximum elastic limit; (4) maximum endurance limit.

If we consider that the stresses are developed rapidly by sudden heating, we must also bear in mind that the application of stress has somewhat the nature of an impact and we must, therefore, add a high impact value to the list of the desirable qualities of a die steel. In most cases the die, during operation, becomes hot. We must, therefore, consider all of these properties from the standpoint of this temperature. In other words, the desired high elastic limit and the desired high impact strength, etc., should be at the elevated temperatures.

Daeves² found that a steel containing 13 per cent Cr, 0.5 per cent Ni, 0.7 to 1.00 per cent C. has a coefficient of expansion less than that of ordinary alloy steels such as studied by Mathews, but Daeves also found this steel to have a lower heat conductivity than carbon steels.

Mathews³ found that for the ordinary types of alloy steels in the heat-treated condition and in the ranges as shown there was very little variation in this property.

Langenberg⁴ found that heat-treated chromium-vanadium steel has maximum notch-bar impact strengths at temperatures between 200° and 500° F. At 1000° F., the highest temperature he investigated, the chromium-vanadium steel was considerably weaker than between 200° and 500° F. He found nickel-chromium steel to have maximum impact strength between 200° and 750° F., its strength apparently holding over a greater range. Of all the steels that he tested the nickel-chromium steel of composition as follows seemed to be the best in this respect: C, 0.39 per cent; Mn, 0.46; P, 0.03; S, 0.025; Si, 0.22; Ni, 3.44; Cr, 1.58.

Moore, Komers and Jasper in their studies of the fatigue of metals,⁵ arrive at the conclusion that for ferrous metals at least the endurance

² K. Daeves: *Präzision*, 1, 270.

³ J. A. Mathews: Coefficient of Expansion of Alloy Steels. *Min. & Met.* (Feb., 1920).

⁴ F. C. Langenberg: Charpy Impact Tests in Steels at Elevated Temperatures. *Jnl. Iron and Steel Inst.* (1923).

⁵ H. F. Moore, J. B. Komers and T. M. Jasper: Fatigue or Progressive Failure of Metals under Repeated Stress. *Proc. Amer. Soc. Test. Mat.* (1922) 22, pt. 2, 266.

limit furnishes the best criterion of resistance to repeated stress with the ultimate tensile strength or the Brinell hardness (which seems to be related to ultimate strength) as a somewhat less reliable index. These investigators call attention to the need of an investigation of the strength of steel under repeated stress and at elevated temperatures.

Work at the General Electric Co. has indicated clearly that there is a relation between the results of notched-bar impact tests and those of notched-bar fatigue tests. Two pieces of steel apparently identical as rated by tensile strength, hardness, elongation, reduction of area and unnotched impact strength may have widely different notched-bar fatigue resistances, and when they do they also have widely different notched-bar impact strengths. The General Electric work shows this on both Izod and Charpy types of impact tests.

PRACTICAL REQUIREMENTS OF A STEEL FOR DIE-CASTING DIES

From the practical standpoint of the user—the die-casting company—the requirements for a steel for dies for casting aluminum, for example, can be listed as follows:

1. Machinability.
2. Stability in heat treatment.
3. Resistance to heat checking.
4. Resistance to deformation, battering, etc.; i.e., hardness.
5. Resistance to cleavage cracking on sudden heating or cooling; i.e., toughness.
6. Resistance to erosive and solvent action of molten aluminum.
7. Cleanliness and uniformity.
8. Cost—producibility, forgeability, etc.
9. Properties at elevated temperatures.

Machinability.—From the standpoint of machinability chrome-vanadium steel seems to be quite satisfactory. Hot-working tungsten steels are much more difficult to machine than the chrome-vanadium steels and are considered just barely passable in the die-casting industry today. Austenitic steels, in general, are out of the question. Possibly the austenitic steels could be made more machinable by the addition of zirconium sulfide, or something of that nature, but it is doubtful whether even if this could be done the steels would be suitable for die-casting dies.

Stability in Heat Treatment.—The standard chrome-vanadium steel used for many years for dies is not satisfactory because of its tendency to warp, grow, shrink and crack during the heat-treating process. The tungsten-chromium type of air-hardening die steels are all quite satisfactory from the standpoint of stability in heat treatment. The tungsten-chromium type of oil-hardening die steels are somewhat dangerous, inasmuch as it is common practice in the manufacturing of die-casting dies to have blocks cut up with very heavy sections next to very thin sections, and with sharp corners between the two, and a steel that requires

oil quenching is liable to crack at these weak points. In general, it seems as though the air-hardening type of steel, whether it contains tungsten or not, is preferable for general purposes.

Resistance to Heat Checking.—The failure by heat checking of die blocks of any one steel seems, to some extent, to be a function of the hardness. In practically all steels tested or used, die life seems to be determined, so far as heat checking is concerned, by the initial hardness. Up to the point where insufficient toughness remains in the steel it seems to be true that the harder the block the longer it will stand up. As the hardness increases there is a gradual and characteristic change in the type or configuration of the heat checks. Hardness, however, is not alone the entire answer, as is indicated by the fact that plain carbon steels of 400 Brinell are inferior to chrome-vanadium steel of the same Brinell hardness. Also, chrome-vanadium steel of 430 Brinell is inferior to chrome-tungsten steel of the same Brinell hardness.

Hardness.—Apart from the relation of hardness to resistance to heat checking, there is required a certain amount of hardness in any block, for service reasons. Dies are made up of moving parts, slides, cores, pins, etc. and usually are hot when in operation. All die parts must be hard enough so that excessive rubbing and scoring and eventual seizing of the parts does not occur. It is possible to have soft main or stationary blocks in a die and hardened moving pieces, but it is preferable to have all the main parts of the die made of the same steel and hardened. Moving parts can be left a bit harder than the stationary parts. All blocks should be hard enough to resist defacement or deformation due to the powerful closing action of the machines when stray pieces of metal are accidentally caught somewhere on the parting faces of the die. About 325 Brinell hardness is as low as is permissible for main blocks in this connection. From the standpoint of resistance to heat checking, the minimum hardness is considerably above 325. For example, it has been found that the hot-working die steels of the chrome-tungsten type develop heat checking rapidly at Brinell hardnesses around 325 and at such hardnesses are apparently inferior to chrome-vanadium steel, whereas if the two steels are compared at Brinell hardnesses of 430 the chrome-tungsten steels are superior to chrome-vanadium steels.

Cleavage Cracking.—This is a difficulty that is not at all serious in the chrome-vanadium steels except when they are left at a Brinell hardness of above 477. In the chrome-tungsten steels cleavage cracking is a serious problem and does not seem to have much relation to the Brinell hardness of the block of steel, but seems to be more closely associated with its macrostructure. Some chrome-tungsten blocks develop serious cleavage cracks at hardnesses as low as 340 Brinell, whereas others of the same analysis do not develop such cracks even at hardnesses as high as 477. In most cases where serious cleavages occur in chrome-tungsten

steel the fracture shows evidence of a fish-scale or a marble structure. As this structure is usually associated with brittleness, it would seem that cleavage cracking is a function of brittleness. The most promising test for this is the notched-bar impact test, and it seems that a steel of a high impact strength at the hardness at which it is to be used is least subject to cleavage cracking.

Erosive and Solvent Action of Molten Aluminum.—Erosion and solvent or soldering action of molten aluminum and its alloys on the die steels is apt to occur at the gates, where the aluminum is at maximum temperature and is made to travel at high velocities across the steel, thus eroding and attacking the steel. A thin oxide layer or an applied layer of graphite prevents this solution attack if the layer can be kept in place and withstand the erosive action of the stream of metal. This erosive action sometimes becomes severe where the molten metal impinges directly upon a steel surface. Resistance of the steel to solvent action is therefore to be preferred although this matter should not be considered of major importance. For years statements have been made that nickel steels are not suitable for dies for aluminum die casting, because of this solvent action. That this is not true is indicated by the promising results obtained by the writer some years ago on several steels containing up to 5 per cent of nickel. The nature of the surface seems to be more important than the composition of the base.

Cleanliness and Uniformity.—Cleanliness and uniformity of a die steel are essential. Segregations and nonmetallic inclusions are starting points for thermal fatigue failures and cleavage cracking. Segregations appearing as hard spots cause great difficulties in die sinking. Internal seams, slits, cracks and other defects must not be encountered at or near the base of a die impression after the greater part of the die sinking has been done. Ample top and bottom discards must be taken from the ingot. Ingots and ingot molds and teeming practice must be regulated to avoid secondary piping, slag inclusions, oxide inclusions, etc. Heating, forging and annealing must eliminate all ingotism and develop uniform structure throughout the section of the finished piece, and must not develop seams, cracks, hammer bursts or other defects.

Cost.—The finished steel for dies for aluminum die casting must be producible at a reasonable price not only from the standpoint of cost of ingredients but also from the standpoint of manufacturing costs in connection with melting, pouring, cogging, discards, chipping, annealing, forging, etc. It seems as though the die-casting trade will stand prices up to 40¢ per pound but not much above that figure, and desires prices considerably below that.

Properties at Elevated Temperatures.—In service, dies for casting aluminum are subjected to temperatures from room temperature or lower (cooling-water temperatures) up to 800° or 900° F., or possibly higher.

Small uncooled parts, for example, near the gate and almost completely surrounded by the aluminum casting, may conceivably become heated almost to the temperature of the incoming metal. Casting temperatures in die casting of aluminum range from 1125° to 1400° F., with the average temperature possibly in the range from 1200° to 1250° F. It is, of course, conceivable that in many cases the surface layers of the die steel, before the body of the blocks of steel can conduct the heat away, become heated to a red heat. For this reason, therefore, red hardness seems to be a desirable property for a die-casting die steel. It is also important that the steel maintain a relatively high elastic limit and impact strength at these elevated temperatures. In other words, the elastic limit and impact-strength curves should preferably have no low areas or inverse deflections from room temperature up to, say, 1000° F.

METHODS OF TESTING PROPOSED NEW DIE STEELS IN DIE-CASTING PLANTS

In plants where the center-gate die-casting machine is used there is a standard part known as the gate former or gate bushing. In these plants often new die steels are tested by making up a few gate formers. The writer has tried out many different kinds of proposed die steel in this way.

Another method of testing a proposed new steel is to insert a block of it in a die. This is common practice in plants that use the split-gate type of machine, which has no gate former. The difficulty in this type of testing is that when a special block is inserted in a given die it is necessary to wait until the die-casting company's customer who owns the die orders a sufficient number of castings to show the actual service the steel will render. This often takes years, and sometimes can never be accomplished because the customer changes his design or his source of supply or discontinues the part.

Another common practice is to use the new steel in the form of a sprue cutter or splitter pin. This is the gate post in many dies on the center-gate machine, and takes the full force of the incoming metal. In most cases, these splitter pins are not very carefully machined, are not held to close dimensions because they do not form a part of the finished casting, are not water-cooled, and are not given close attention. In general, it is difficult to obtain any important information in tests of sprue cutters, except from the standpoint of the soldering action of the aluminum on the proposed die steel. Even this is sometimes at fault because often it is desirable to have the metal stick to the sprue cutters to some extent, and no effort is made to keep the sprue cutter coated with graphite and oil to prevent the solvent action. If the sprue cutter were a part of the die, the attention given it would be entirely different, and possibly the net result on the steel would differ considerably.

A method of testing sometimes used is known as "total immersion." A block, for instance a 2-in. cube, of the proposed die steel is dropped into a molten bath of aluminum together with a similar block of a known steel and allowed to remain in the molten aluminum for a number of days. When it is taken out the aluminum is cleaned off as well as possible and the weight losses are determined. This is truly a solvent action test and therefore is not indicative of what the steel might do in resisting heat checking. It is well known that cast iron is much less soluble than steel in molten aluminum; therefore, although cast iron is not a suitable material for die-casting dies for aluminum, it stands up much better than any of the standard die steels in this total immersion test. It is interesting to note, however, that one or two special steels have seemed to stand up better in aluminum dies than chrome-vanadium, and also to have less tendency to go into solution in molten aluminum in this total immersion test than chrome-vanadium steel. It is the writer's belief, however, that these results are not important and that normally the total immersion test is not of much value in evaluating different proposed die steels.

A proposed method for testing new die steels might be termed the "alternate immersion method" with water cooling. In this test the samples of die steel are mounted on a crank arm so as to be alternately dipped into and taken out of a bath of molten aluminum eight or ten times per minute. The specimens are drilled so that water may be circulated through them to maintain them at a fairly low temperature. A counter on the crank arm makes it possible to determine the total number of cycles gone through until the time that heat checking begins to appear. Ten or twelve different steels can be tested at once in this manner. The test is not a duplication of the conditions in a die-casting die, because the molten metal does not strike the specimens as suddenly and the contact between the molten metal and the steel is not as intimate as when the molten metal is forced against the steel under considerable pressure and with considerable velocity.

METHODS OF LABORATORY TESTING

A die-casting company wants to know a number of things about a new steel before putting it to a test in service. This information should be supplied by the mill proposing the steel, and can be determined by laboratory methods of testing, somewhat as follows:

The various transformations occurring in the steel upon heating and cooling are first to be determined, which can be done easily by the use of a Rockwell dilatometer furnace. From the transformations on heating and cooling as shown by the dilatometer curves the proper heat-treatment temperatures for the proposed steel can be selected. From a heat-treating standpoint, it is desirable next to know whether or not small and large pieces of the steel will heat-treat at the same temperature or

whether higher temperatures will be required for the large pieces. In other words, the depth of hardening of the steel is to be determined, and this usually is done by the heat treatment of a small piece and a large piece simultaneously and checking up the finished hardness of the pieces. In this, of course, it is to be remembered that small pieces do not have to be soaked at temperature as long as the large pieces, but the actual temperature should be the same irrespective of the size of the piece.

The next thing to determine is the amount of dimensional change occurring in the steel as a result of various heat treatments. This can be carried out by the actual heat-treating of U-shaped blocks of steel. Such blocks of steel as machined up are carefully measured then given the quenching treatment as determined by the previous test; again carefully measured, then drawn and again measured; completely annealed and again measured, then rehardened and again measured, and, finally, drawn again and measured.

Other laboratory tests to be carried out are Brinell hardness, tensile strength and elastic limit, and notched-bar impact tests at room temperature and at 200°, 350°, 500°, 650° and 800° F.

Finally the proposed steel should be examined metallographically to see that it is clean, free from nonmetallic inclusion and uniformly free from serious segregation; also, to see that it has a uniform grain structure, free from abnormally large grains, outstanding grain boundaries, and so forth.

TESTS OF NEW COMPOSITIONS

In cooperation with the Vanadium Alloy Steel Co. a number of proposed compositions were studied. Steels of five different analyses were melted and forged into 4-in. cubes. All steels after forging were annealed by sealing in a tube and cooling slowly from 1575° F. Decarburized surfaces were then removed by machining and the blocks heat-treated by cooling in still air from 1900° F. The blocks were then compared for the degree of scale present.

The No. 527 steel was found to possess a thin scale, which was very adherent and difficult to remove. Steel No. 528 had a heavy, adherent scale, which also was hard to remove. No. 531 had a thin adherent scale less in amount than that observed on the No. 527 steel and easier to remove. Steel 532 possessed a heavy adherent scale difficult to remove, while steel 533 had a heavy scale, which was loosely adherent and easy to remove. It was apparent that steel 531 possessed the best properties in this regard.

Brinell tests were taken to observe the hardening properties of the various steels, and these results, together with the compositions of the metals, are recorded on the attached charts (Figs. 1 to 5). Hardness tests after drawing to 1075° F. are also indicated.

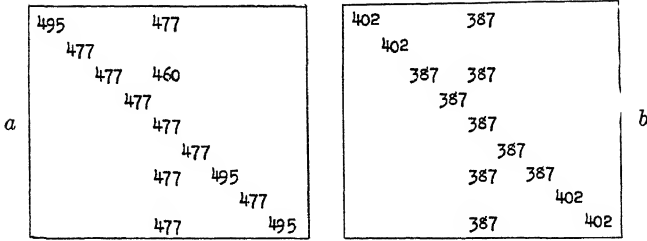


FIG. 1.—No. 527 STEEL; 4-INCH CUBE.

a. Air-cooled from 1900° F. *b.* Air-cooled from 1900° F. Drawn 1075° F. 5 hours. Analysis: carbon, 0.34 per cent; silicon, 0.96; manganese, 0.33; sulfur, 0.026; phosphorus, 0.018; tungsten, 5.36; chromium, 5.11; cobalt, 0.50.

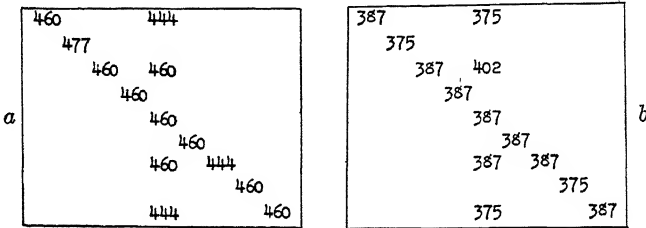


FIG. 2.—No. 528 STEEL; 4-INCH CUBE.

a. Air-cooled from 1900° F. *b.* Air-cooled from 1900° F. Drawn 1075° F. 5 hours. Analysis: carbon, 0.28 per cent; silicon, 1.27; tungsten, 0.99/1.03; chromium, 4.76/4.78; molybdenum, 1.50.

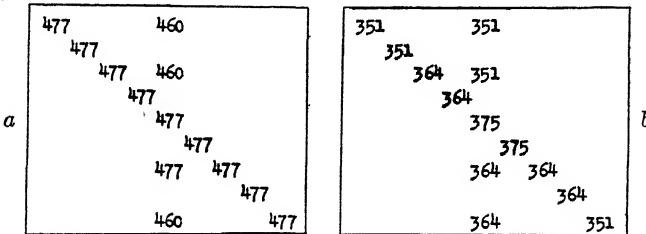


FIG. 3.—INGOT 531; 4-INCH CUBE.

a. Air-cooled from 1900° F. *b.* Air-cooled from 1900° F. Drawn 1075° F. 5 hours.

| | Analysis, Per Cent | |
|-----------------|--------------------|-------------|
| | Desired | Actual |
| Carbon..... | 0.35 | 0.33 |
| Sulfur..... | | 0.048/0.051 |
| Chromium..... | 5.00 | 4.52/4.56 |
| Tungsten..... | 1.00 | 1.15 |
| Molybdenum..... | 1.00 | 1.06 |
| Nickel..... | 1.50 | 1.45 |

Forgings for movement and tensile tests were made from the five blocks used for hardness tests, the forgings for movement tests being finished to $5\frac{1}{8}$ in. round by $1\frac{1}{8}$ in. thick and forgings for tensile-test specimens to $\frac{7}{8}$ in. square by 14 in. long. All forgings were then annealed at 1575° F.

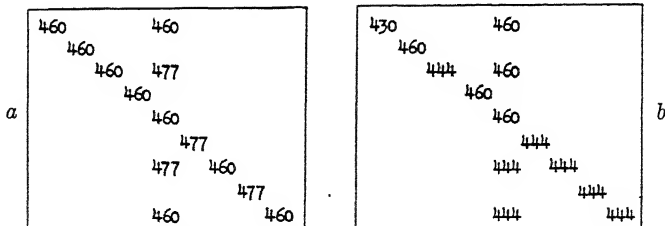


FIG. 4.—INGOT 532; 4-INCH CUBE.

a. Air-cooled from 1900° F. b. Air-cooled from 1900° F. Drawn 1075° F. 5 hours.

| | Analysis, Per Cent | |
|-----------------|--------------------|-----------|
| | Desired | Actual |
| Carbon..... | 0.35 | 0.41/.42 |
| Silicon..... | | 0.43 |
| Tungsten..... | | 0.14 |
| Chromium..... | 5.00 | 4.48/4.50 |
| Molybdenum..... | 2.00 | 2.10 |
| Nickel..... | | 0.08 |

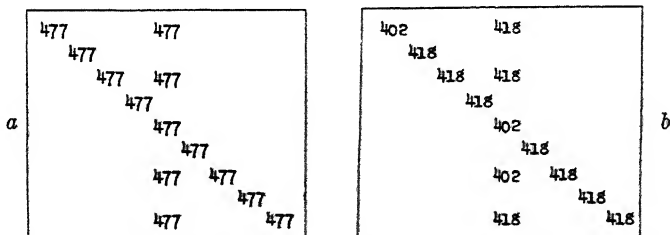


FIG. 5.—INGOT 533; 4-INCH CUBE.

a. Air-cooled from 1900° F. b. Air-cooled from 1900° F. Drawn 1075° F. 5 hours.

| | Analysis, Per Cent | |
|---------------|--------------------|-----------|
| | Desired | Actual |
| Carbon..... | 0.35 | 0.40/0.41 |
| Silicon..... | | 0.24 |
| Tungsten..... | 4.00 | 3.75/3.77 |
| Chromium..... | 5.00 | 4.64/4.66 |

The tensile-test specimens were machined to 0.512 in. in order to allow for movement and removal of surface after heat treatment. They were then heated to 1900° F., air-cooled and drawn for 1 hr. at 1075° F. After this treatment they were cleaned up and finished to 0.505 in. The results of the tensile tests are shown in Table 1.

TABLE 1.—*Results of Tensile Tests*

| Steel | Original Area, Sq. In. | Yield Point, Lb. | Maximum Load, Lb. | Yield Point, Lb. per Sq. In. | Tensile Strength, Lb. per Sq. In. | Elongation | | Reduction of Area, Per Cent | Brinell Hardness | Fracture |
|-------|------------------------|------------------|-------------------|------------------------------|-----------------------------------|------------|----------|-----------------------------|------------------|-------------------------------|
| | | | | | | In. | Per Cent | | | |
| 527 | 0.2003 | 52,700 | 55,720 | 263,100 | 278,200 | 0.16 | 8.0 | 19.2 | 512 | Fine granular with silky lip. |
| 528 | 0.2003 | 51,800 | 55,280 | 258,600 | 276,000 | 0.24 | 12.0 | 41.9 | 532 | Silky ½ cup. |
| 531 | 0.2003 | 47,860 | 49,480 | 238,930 | 247,000 | 0.28 | 14.0 | 44.9 | 477 | Silky ½ cup. |
| 532 | 0.2003 | 52,500 | 56,030 | 262,100 | 279,700 | 0.07 | 3.5 | 5.1 | 532 | Fine granular with silky lip. |
| 533 | 0.2003 | 49,100 | 51,640 | 245,100 | 257,800 | 0.20 | 10.0 | 30.9 | 512 | Fine granular with silky lip |

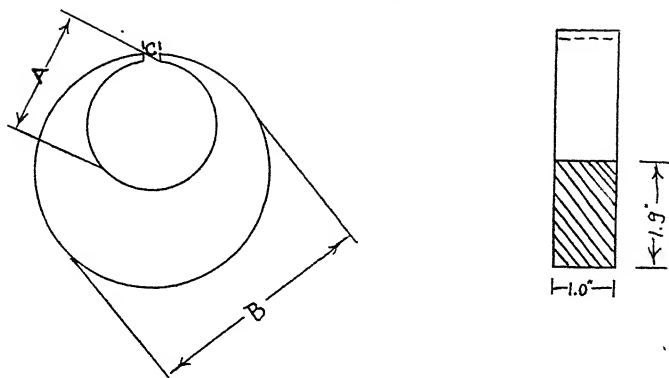
The movement test specimens were normalized in pitch coke at 1250° F. before any measurements were taken. They were then measured; hardened by packing in pitch coke and heating to 1900° F., then cooled in still air. After remeasuring they were drawn at 1075° F. and again measured. The results of these tests are given in Table 2.

IMPACT STRENGTHS AT ELEVATED TEMPERATURES

As already mentioned, die-casting dies are subjected to sudden stresses due to local and sudden heating. In service, die-casting dies for aluminum operate at temperatures varying from cold up to as high as 800° or 900° F., or possibly higher. Die steels fail by developing large cracks or fine heat checks. Failures are accentuated by the presence of surface imperfections such as scratches, indicating that the notch effect must be taken into consideration. It would appear, therefore, that a good steel for dies for casting aluminum should have a relatively high impact strength at elevated temperatures, and that there should be no low areas in the impact-strength temperature curve for the range from room temperature up to 800° or 1000° F.

Of the number of different steels made up experimentally by the Vanadium-Alloys Steel Co., two steels, Nos. 528 and 531, seemed most promising from the results of the heat-treating, scaling and dimensional change tests. Therefore Charpy impact-strength temperature curves were plotted for these two steels.

Fifteen to eighteen Charpy impact-test specimens in the machined and heat-treated condition were supplied by the Vanadium-Alloys Steel

TABLE 2.—*Results of Movement Tests*

| Heat-treated Condition | | Normalized | Hardened | Drawn | Variation |
|------------------------|---|------------|----------|----------|-----------|
| No. 527 | A | 2.8992 | 2.9000 + | 2.9030 + | +0.0038 |
| | B | 4.9957 | 4.9975 + | 4.9995 + | +0.0038 |
| | C | 0.5020 | 0.5195 + | 0.5200 + | +0.0180 |
| No. 528 | A | 2.9031 | 2.9022 - | 2.9042 + | +0.0011 |
| | B | 4.9930 | 4.9905 - | 4.9933 + | +0.0003 |
| | C | 0.5018 | 0.5070 + | 0.5085 + | +0.0067 |
| No. 531 | A | 2.9114 | 2.9032 - | 2.9044 + | -0.0070 |
| | B | 5.0082 | 5.0023 - | 5.0032 + | -0.0050 |
| | C | 0.5180 | 0.5115 - | 0.5120 + | -0.0060 |
| No. 532 | A | 2.8995 | 2.8975 - | 2.8980 + | -0.0015 |
| | B | 4.9971 | 4.9981 + | 4.9997 + | +0.0026 |
| | C | 0.5021 | 0.5014 - | 0.5012 - | -0.0009 |
| No. 533 | A | 2.9003 | 2.8984 - | 2.8980 + | -0.0023 |
| | B | 5.0025 | 5.0037 + | 5.0027 - | +0.0002 |
| | C | 0.5022 | 0.5000 - | 0.5005 + | -0.0017 |

Co. for each of the steels 528 and 531, for a chrome-vanadium steel and for No. 527 steel. Additional sets of Charpy impact-test specimens in the machined and heat-treated condition were supplied by the Hoover Company for each of two additional steels.

Testing was carried out on an Amsler impact-testing machine of the Charpy type with a pendulum with a delivering capacity of approximately 120 ft-lb. of energy. One-half of each of the broken specimens was carefully tested for Rockwell hardness. Tests were made by the Hoover Company on two more steels and their results are included in this

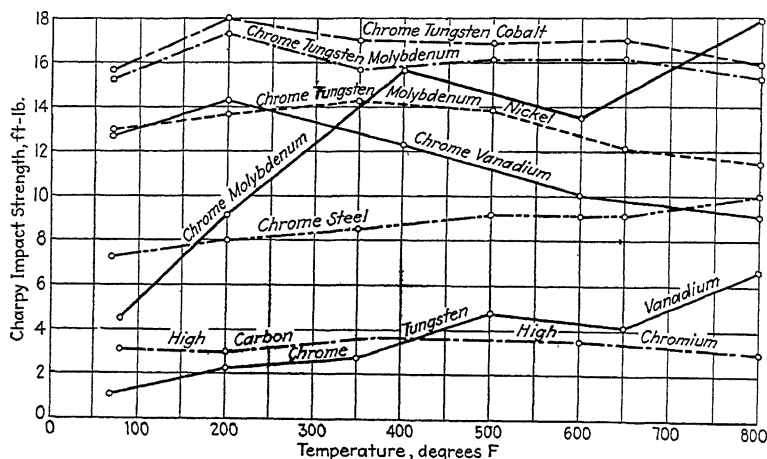


FIG. 6.—IMPACT TESTS OF STEELS FOR DIE-CASTING DIES AT ELEVATED TEMPERATURES.

paper. All results and analyses are shown on Table 3 and plotted on Fig. 6.

The average Rockwell hardness of the No. 527 specimens was slightly lower than that of the No. 528 and No. 531 specimens. Also, the 531 specimens were slightly harder than the 528 specimens. It is significant that the impact strengths are lower for the material having higher Rockwell hardness. The considerably lower impact strength, however, for steel No. 531 as compared to No. 528 seems to be more than could be accounted for by the slight variation in Rockwell hardness. The fact that the impact strength decreases continuously from a temperature of 350° in steel No. 531 seems to be significant also as compared to steel No. 528. In general, it might be concluded that so far as impact-strength temperature is concerned steel 528 is the equal of steel 527.

The chrome-molybdenum and the chrome-vanadium alloy steels have the greatest variation in impact strengths, the latter having its maximum strength of 14.33 ft.-lb. at 200° F. and falling off consistently to its minimum of 9.17 ft.-lb. at 800° F. The chrome-molybdenum shows a decided increase in impact strength from room temperature to 400° F., but at 600° F. the impact strength has fallen off appreciably.

TABLE 3.—*Impact Tests of Die-casting Die Steels at Elevated Temperatures*

| Temperature, Deg. F. | Chrome-vanadium | | Chrome-tungsten-molybdenum | | Chrome-tungsten-molybdenum-nickel | | Chrome-tungsten-cobalt | | Chrome-tungsten-vanadium | | Chrome | | Chrome-molybdenum | | High-carbon, High-chrome | |
|----------------------------|-----------------|---------|----------------------------|---------|-----------------------------------|---------|------------------------|---------|--------------------------|---------|-----------------|---------|-------------------|---------|--------------------------|---------|
| | Impact Strength | | Impact Strength | | Impact Strength | | Impact Strength | | Impact Strength | | Impact Strength | | Impact Strength | | Impact Strength | |
| | Ft.-lb. | Average | Ft.-lb. | Average | Ft.-lb. | Average | Ft.-lb. | Average | Ft.-lb. | Average | Ft.-lb. | Average | Ft.-lb. | Average | Ft.-lb. | Average |
| 70-80 | 14 | 12.07 | 13 | 13 | 16 | 23 | 8 | 1.05 | 7.0 | 5 | 3.0 | 3.5 | 3.0 | 3.5 | 3.0 | 3.17 |
| | 11 | | 13 | | 10 | 16 | 16 | | 7 | 3.5 | 3.5 | | 4.5 | | 3.0 | |
| | 13 | | 20 | | | | | | 8 | | | | | | 3.0 | |
| 200 | 10 | 14.33 | 15 | 17.33 | 14 | 17 | 16.5 | 3.0 | 8.5 | 8.5 | 3.5 | 9.17 | 3.5 | 3.0 | | |
| | 12 | | 15.5 | 13.5 | 13.5 | 20.5 | 20.5 | 2.50 | 8.0 | 10.0 | 2.0 | | | | | |
| | | | | | | | | | | | | | | | | |
| 350 | | | 15 | 15.67 | 13 | 17.5 | 16.5 | 2.75 | 8.5 | | | | | | | |
| | | | 17 | 14 | 14.33 | 16.5 | 17.0 | 2.5 | 8.5 | | | | | | | |
| | | | 15 | | 16 | 17.0 | | | 8.5 | | | | | | | |
| 400 | 13 | 12.5 | | | | | | | | | | | | | | |
| | 12.5 | 12.33 | | | | | | | | | | | | | | |
| | 11.5 | | | | | | | | | | | | | | | |
| 500 | | | 16.5 | 16.17 | 15.5 | 16 | 16.5 | 5 | 9.0 | 14.5 | 3.0 | 15.67 | 3.5 | 3.67 | | |
| | | | 10 | 13 | 13.83 | 18 | 16.83 | 5 | 9.5 | 17.0 | 4.5 | | | | | |
| | | | 16 | 13 | 10.5 | 10.5 | 4.25 | | 9.0 | 15.5 | 3.5 | | | | | |
| 600 | 9.5 | 10.0 | | | | | | | | | | | | | | |
| | 10.5 | | | | | | | | | | | | | | | |
| | 10.0 | | | | | | | | | | | | | | | |
| 650 | | | 16.5 | 16.17 | 12 | 15 | 16.5 | 4.5 | 9 | 13.5 | 3.5 | 13.5 | 3.5 | 3.5 | | |
| | | | 17.0 | 12 | 12.17 | 16.5 | 17.00 | 4.16 | 9.25 | 13.0 | 3.5 | 14.0 | 3.5 | | | |
| | | | 16.0 | 12.5 | 12.5 | 19.5 | 4.25 | 9.0 | 9.0 | 14.0 | 3.5 | | | | | |

The chrome-tungsten-vanadium steel showed abnormally low impact strengths throughout, which may be attributed to some treatments of the steel prior to the making of the impact-test bars in which some fish-scale or marble structure had developed. This type of steel oil-quenched, not air-hardened, from 2100° F. and drawn is often used rather successfully for a hot-working die steel.

The high-carbon, high-chrome steel also showed abnormally low impact strengths throughout. This steel oil-quenched from a lower temperature would probably have yielded higher impact strengths.

ACKNOWLEDGMENTS

The author wishes to acknowledge the assistance given by Mr. J. P. Gill of the Vanadium-Alloy Steel Co. and Mr. R. Roshong of the Hoover Company in this work, and to thank them for the permission to publish these results.

DISCUSSION

(John A. Mathews presiding)

J. A. MATHEWS,* New York, N.Y.—There is one point that I wish Mr. Tour had discussed, and perhaps he will at some later time; that is, the effect of long holding upon his steels before making high-temperature impact tests. These impact pieces seem to have been heated up and immediately broken. There is a great difference between different steels as to the effect of long time holding at heat. We have some results of a 5 per cent chromium steel with tungsten or molybdenum additions where this is well illustrated. If we may assume that operating at elevated temperatures that are frequently attained is equivalent to a long, continuous holding for hours, we find that the chromium-tungsten steels show a marked falling off in impact resistance, while the chromium-molybdenum steels do not.

Heat checking may be a function of temper brittleness induced by frequent heating up to a range of 800° to 900° F., and after a die has become temper brittle because of repeated superficial tempering, the checking starts and after that cracks propagate rapidly. A 5 per cent chromium, 1 per cent tungsten steel, heat-treated and tempered to 300 Brinell, showed initially 91 ft.-lb. in the impact test, but after holding the same steel for 1000 hr. at 850° F., it showed but 14 ft.-lb., a very serious drop. A similar chromium-molybdenum steel tempered to 370 Brinell showed initially 74 ft.-lb. and 72 ft.-lb. after 1000 hr. at 850° F. There is therefore a difference in susceptibility to temper brittleness in chromium steels containing tungsten or molybdenum, notwithstanding that these elements are usually considered substitutes for one another, and I feel that the impact tests reported by Mr. Tour would have been of more practical importance had they been made after long holding at temperature.

There is another point in connection with one of the steels described by Mr. Tour, as shown on the hardness charts for tests made on 4-in. cubes. One of his steels showed exactly the same hardness after tempering at 1075° as it showed in the as-quenched condition. It is suggested that that steel probably contained a great deal of retained austenite and that a secondary hardening occurred on tempering at 1075° F. I cannot help but think that at some other temperature, either above or below 1075°, the hardness would not be as great as it was originally.

* Vice President, Crucible Steel Co. of America. Died Jan. 11, 1935.

R. G. ROSHONG,* North Canton, Ohio.—I believe that Mr. Tour's paper ought to foster some closer relationships between the producers and users of die steels.

I have followed with considerable interest the results of the impact test, and it is our feeling that the impact tests at elevated temperatures do give some reliable indications as to the possibility of the steel cracking during heat-treatment. However, as Mr. Tour has stated, they do not always give reliable indications as to whether the steel is going to heat-check.

On Fig. 6 the impact values for the high-carbon, high-chrome steel were quite low as compared to other steels; nevertheless that steel under proper heat-treatment gives good life as far as heat checking is concerned. I can recall an instance of a die checking very badly opposite the sprue in making a 3½-lb. casting from the 10 per cent silicon-aluminum alloy, and this die lasted only about three weeks. An insert was made of a piece of high-carbon, high-chromium steel containing 3 per cent cobalt, air-quenched from 1850° F., and drawn to 1050° F. That piece was in service for four years without any heat checking or washing. Since that time, larger inserts have been made of this steel, up to 6 in. in diameter, with similar results.

One other item is of interest—the temperature the die attains. The temperature at which the molten aluminum is shot into the die varies anywhere from 1150° to perhaps 1300°, for the more highly alloyed aluminum alloys. Something was mentioned about the die-face temperature rising to 800° F. I have never seen so high a temperature in any of our dies. We have a delicate surface pyrometer which has indicated temperatures as high as 475 to 500, and upon inserting a thermocouple between the dies, when the blocks were closed after thorough heating, we found similar results.

Therefore, I would say that the block in general is operating within these temperature ranges. However, we must concede that there is a considerably higher temperature on a very thin skin for a short time which would lead us to believe that the hardness should be drawn from the steel. However, Rockwell hardness or Brinell measurements do not show that to be true. It probably would take a more delicate instrument to tell whether the steel is being drawn back.

I think that we will find sooner or later that there is some definite physical property tied up with this heat-checking phenomenon and it would be desirable if a simple, or relatively short test could be developed to predict resistance to heat checking, since most die-casting companies cannot afford to try out various types of steels, on an expensive die, with the possibility of obtaining early development of heat checking.

G. M. ROLLASON,† Garwood, N. J.—Mr. Tour is to be congratulated on formulating, for the benefit of the industry at large, what hitherto has been more or less a matter of hearsay. As Mr. Roshong says, it will probably result in a good deal better coordination between the producers of steel and the users of that steel.

However, there is one point on which some of us do not quite agree with Mr. Tour, that is, in connection with the No. 6 property of the steel, the erosion, or washing. The chances are, I think, that the other companies have been improving and we see that more now than we did. But I think that the steel companies can profitably improve the steel in its resistance to erosion and gate washing.

A. L. DAVIS,‡ Waterbury, Conn.—Mr. Roshong desires a *short-time* test to determine the degree of susceptibility of a steel to heat checking when used in dies for die casting. I suggest the use of a surface grinder, using a small sample of the unknown steel in comparison with similar samples of two or more steels whose performance in

* Engineering Laboratories, The Hoover Co.

† Aluminum Company of America.

‡ Scovill Manufacturing Co.

die-casting dies is already known from actual service. The surface cracks that can be developed in any hardened steel by grinding under sufficiently abusive conditions are akin to the heat checks produced by hot-work, as in die-casting dies. The more susceptible a steel is to grinding checks, the more rapidly it should develop heat checks in dies. The difference in steels in resisting development of grinding checks is illustrated in the Carpenter Steel Company's booklet of 1931 on Tough Carbon Steel, page 18.

S. TOUR (written discussion).—The suggestion by Dr. Mathews that heat checking may be a function of temper brittleness induced by frequent heating up to a range of 800° to 900° F. is worthy of serious thought, and his suggestion that impact tests should be made after long holding at temperatures is indeed a good one. To the writer's knowledge no such tests have yet been made.

Mr. Roshong points out the low impact values obtained on a straight high-carbon high-chrome steel and states that such a steel however does give good life as far as heat checking is concerned and cites an instance of this in connection with such a steel containing 3 per cent of cobalt. Of course one cannot assign low impact values obtained on a plain high-carbon high-chrome steel to a high-carbon high-chrome cobalt steel. Also, it is entirely possible that the particular impact specimens tested were not in the same condition as to hardness and brittleness as the die blocks referred to by Mr. Roshong.

Mr. Roshong questions the temperatures of 800° F. and refers to readings taken with surface thermocouples being below 475° to 500° F. It must be realized that there is considerable time lag between the making of a casting and the obtaining of a reading on a die surface and that during this time the surface is rapidly being cooled by the conduction of the entire mass of steel below the surface. In thermal or heat checking we are concerned with the very surface and the maximum temperature which this surface obtains with respect to the mass of steel below it. In other words, we are concerned primarily with the temperature gradient and temperature differential between surface and center. For a center or body temperature of 500° a surface temperature of 800° would not be as harmful and productive of heat checking as if the body temperature were only 300°.

That steels of the chrome-vanadium type drawn at 800° F. before being put in use are softened on the surface by use has been fully demonstrated in practical experience on hundreds of dies.

Mr. Davis suggests the use of a surface grinder for a short-time test to determine susceptibility to heat checking. Such tests are quite useful on very hard tool steels, Brinell hardnesses of over 500° or 600°, but do not offer much promise on steels in the 400° to 500° range of hardness. Surface grinding of hardened die-casting die blocks is common practice in the die-casting industry. Very, very seldom do any checks develop from such grinding.

Some years ago the writer suggested a method of accelerated laboratory testing by the use of an arc repeatedly drawn between electrodes near the surface of a water-cooled block, but so far as is known no such test has been tried out in practice. Another possible method of test recently suggested is repeated contacting of the surface of a cooled block with a red hot disk of a heat-resistant alloy. It is hoped that some such test will be developed soon.

Hardening and Tempering of Steels Containing Carbides of Low Solubility, Especially Vanadium Steels

By E. HOUDREMONT,* MEMBER A.I.M.E., H. BENNEK AND H. SCHRADER

(New York Meeting, February, 1935)

THE different influences exerted by the various alloying elements in iron and iron-carbon alloys give rise to a great number of complexities, which are difficult to grasp. It is important therefore to study any systematic relations that may exist between the effects exerted by the various alloying elements, in order to obtain a general classification and thus a clearer conception of the nature of alloy steels.

A systematic survey of the alloys of iron, based on an investigation of the binary equilibrium diagrams, was recently published by Wever. Although his work deals little with properties of importance in works practice, its purpose being rather to point out the theoretical agreement among the types of binary equilibrium diagrams and the position of the alloying elements in the periodic system (atomic radii, etc.), the classification proposed nevertheless also suggests relationships among the properties of the alloys in question, even though the alloys may contain carbon in addition to iron and the alloying element.

Wever divided the alloys of iron into one group exhibiting an open or enlarged gamma field and another exhibiting a closed or restricted gamma field, with both groups capable of further subdivision depending upon whether a continuous series of solid solutions is formed, or, owing to the separation of compounds, etc., only a limited series.

Thus all alloying elements which with iron form a closed gamma field, a "gamma loop," produce alloys that beyond the composition corresponding to the greatest extent of the gamma loop are composed of ferrite alone at all temperatures. Alloys of this composition accordingly are not susceptible to ordinary heat treatment because of the lack of transformations. Steels of this class may thus be divided into steels that contain less than the critical amount of alloying element, and are subject to heat treatment, and those that contain more than the critical amount of alloying element and are not subject to heat treatment. Thus chro-

Manuscript received at the office of the Institute March 19, 1934. Edited and rewritten in part by Robert F. Mehl, Director, Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

* Assistant Manager, Krupp Steel Works, Essen, Germany.

mium steels are now classified as pearlitic, semiferritic, or ferritic,¹ a classification that can be adopted for all elements that have this type of equilibrium diagram. These terms have already become associated with definite conceptions in regard to properties, production methods, etc.²

Much the same is true of elements that enlarge the gamma field; the austenitic alloys, stable at room temperature, also exhibit regularities in behavior, both with respect to properties and manufacture.

Apart from the foregoing classification, it is possible for alloys containing carbon to form another large group comprising the elements that

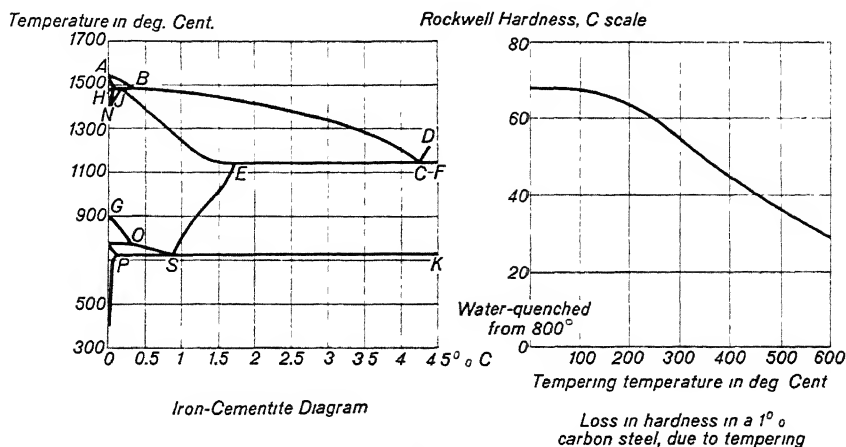


FIG. 1.—IRON-CARBON SYSTEM AS EXAMPLE OF SYSTEM WITH ONE ELEMENT POSSESSING TWO MODIFICATIONS, WHICH RESPECTIVELY EXHIBIT DIFFERENT SOLID SOLUBILITIES FOR A SECOND ELEMENT OR COMPOUND.

form special carbides, such as chromium, molybdenum, tungsten, vanadium, titanium, tantalum, etc. The similarity that exists between these elements is shown by the fact that all form a closed gamma field in the absence of carbon. Therefore it would appear desirable to examine the influence of several of these carbide-forming elements; a particularly suitable field for these investigations appears to be that of the phenomena occurring during the operations of hardening and tempering. Two possibilities obtain in the hardening of alloys:

1. The solvent metal possesses two modifications; the solute element dissolves to different degrees in these two modifications. Upon transformation on cooling from the phase type stable at a high temperature to that stable at low temperature, a new phase may not be given the opportunity to separate freely, and tempering of the quenched alloy leads to a

¹ E. Houdremont: *Stahl und Eisen* (1930) **50**, 1517; *Rev. de Met.*

² Reference of footnote 1.

series of changes in properties similar to those shown in Fig. 1. Example: The Fe-C system.

2. The solvent metal possesses but one modification; the solubility of the solute element in this modification increases upon increasing temperature. Rapid cooling from a high temperature will retain a supersaturated solid solution, which upon tempering will precipitate a

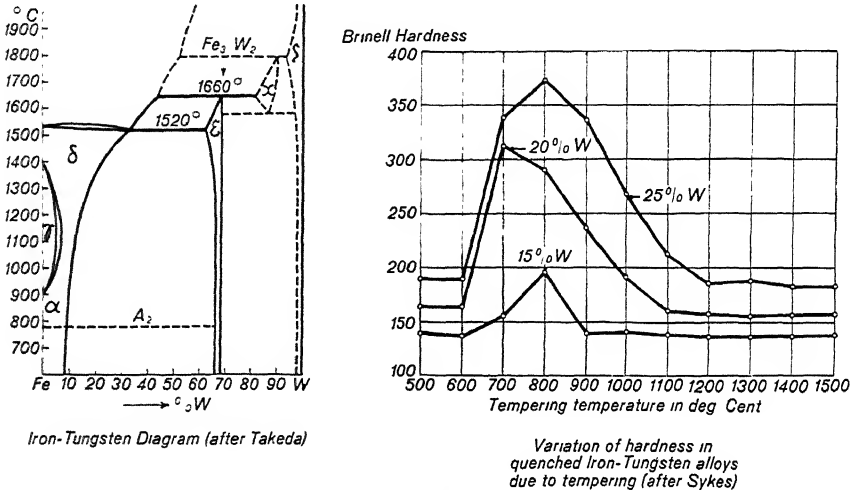


FIG. 2.—IRON-TUNGSTEN SYSTEM AS EXAMPLE OF POSSIBILITY OF HARDENING DUE TO DECREASING SOLUBILITY WITH DECREASING TEMPERATURE AND SUBSEQUENT PRECIPITATION OF CONSTITUENTS FROM SUPERSATURATED SOLUTION.

new phase and cause hardening, as shown in Fig. 2. Examples: The solution of Fe₃C in α Fe; the Fe-Mo and Fe-W systems.

There is no reference in the literature to a possible combination of these two processes, caused by the presence of both an allotropic transformation, and also an increasing solubility of a separate phase with increasing temperature. Such a changing solubility is exhibited by austenite and iron carbide in the iron-carbon system, shown by the line ES.

TABLE 1.—Precipitation-hardening of Austenitic Chromium-nickel Steel Induced by Tempering

| C 0.50 | Si 1.80 | Mn 0.75 | Cr 15 | Ni 13 | W 2 | Yield Point, Kg. per Sq. Mm. | Tensile Strength, Kg. per Sq. Mm. |
|------------------------------------|------------|------------|----------|----------|--------|---------------------------------|--------------------------------------|
| Water-quenched from 1200°..... | | | | | | 33 | 85 |
| Subsequently tempered at 700°..... | | | | | | 50 | 90 |

The existence of the line ES is revealed in the hardening of Fe-C alloys by the fact that hypereutectoid steels quenched from temperatures above the line ES exhibit an increased depth of hardening and a greater

amount of retained austenite, owing to the increased solubility of the carbide. In tempering, however, no special effect is to be expected when quenching has been performed from above the line ES , instead of from a temperature just above the eutectoid horizontal, since the new phase is the same in both cases; namely, Fe_3C .

Although the increasing solubility of Fe_3C in austenite with increasing temperature exerts an influence on the mechanism of hardening but not on that of tempering, such is not the case in the presence of elements forming special carbides in addition to iron carbide (as, for instance, carbides of tungsten, vanadium, titanium, chromium, etc.). These carbides have special solubilities in the austenite field, shown by special solubility curves, so that after transformation is complete the special carbide will progressively go into solution with increasing temperature. In purely austenitic steels precipitation-hardening occurs by quenching and tempering through the action of such carbides, as shown in the unpublished investigations by Houdremont and Kallen (Table 1), and in the more recent work of Greulich.³

In regard to high-tungsten steels, it can further be shown that so long as quenching is carried out from normal temperatures (about $760^{\circ}C$.) the depth of hardening decreases with increasing tungsten content, owing to the abstraction of carbon from the matrix through the formation of tungsten carbides which are insoluble at normal quenching temperatures. But with increasing quenching temperatures the depth of hardness increases and from a certain quenching temperature upward exceeds the maximum depth obtainable with plain car-

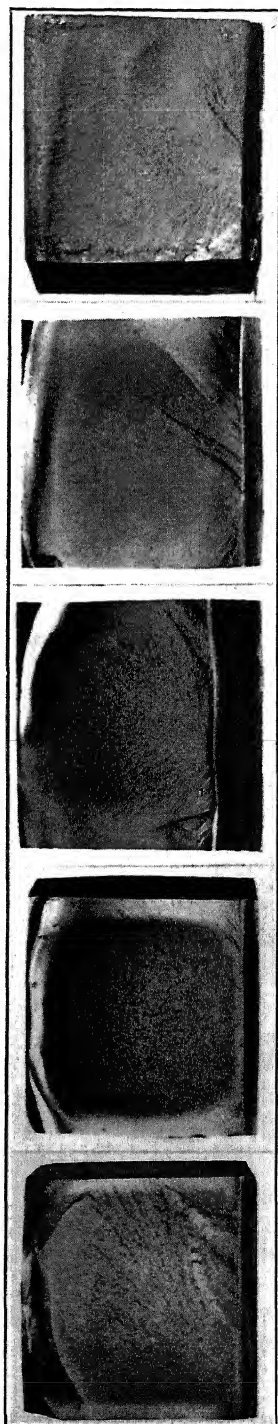


FIG. 3.—DEPTH OF HARDNESS OBTAINED IN TUNGSTEN-ALLOYED TOOL STEEL BY QUENCHING FROM VARIOUS TEMPERATURES. SECTION 40 SQ. MM.

³ Greulich: *Archiv f. d. Eisenhüttenwesen* (1931/32) 5, 323.

bon steels (Fig. 3). Thus, by alloying a steel with tungsten and quenching from a low temperature, it is possible to produce a steel with a very thin hardened layer. With increasing quenching temperature and consequently increasing proportion of carbon dissolved in the form of the stable carbide, greater depth of hardness will be secured.

At the same time steels containing such carbides exhibit great indifference to overheating. Whereas plain carbon steel, quenched from a temperature only 60° higher than its normal quenching temperature, develops a coarse grain, steels containing such carbides will not show exaggerated grain growth when subjected to considerably higher temperatures because the finely dispersed carbide inhibits the growth of the austenite grains.

Since the solution of these carbides increases in amount with rising temperature and in some instances becomes complete only near the solidus curve, it is of interest to ascertain whether the separation of the carbides during the tempering process nevertheless takes place at the same temperatures as iron carbide. Observations available at present appear to indicate that the temperature at which precipitation takes place depends upon the temperature of solution (Table 2).

TABLE 2.—*Relation between Quenching and Precipitation Temperatures in Various Systems Capable of Precipitation-hardening*

| System | Quenching Temperature, Deg. C. | Precipitation Temperature, Deg. C. |
|-------------------------------------|--------------------------------|------------------------------------|
| Duralumin. | About 500 | Room |
| Iron-beryllium | 1000-1200 | 450-600 |
| Iron-titanium. | | |
| Iron-tungsten. | 1300-1400 | 700-900 |
| (Iron-molybdenum similar) | | |

On studying the tungsten steel mentioned above during the tempering operation, it is found that an increase in quenching temperature and therefore in the quantity of dissolved carbide increases the stability of hardness upon tempering (Fig. 4). Whereas no essential difference is to be found between tungsten steel and carbon steel when quenched from normal temperatures, tungsten steel when quenched from higher temperature exhibits a greater stability of hardness upon tempering than carbon steel. This cannot be ascribed to an increased retention of austenite and consequent transformation of this residual austenite upon tempering, because repeated tempering at increasing temperatures would progressively decompose the residual austenite into martensite, which in turn would soften, not harden; all samples in the present study were tempered eight

times. It is reasonable to suppose that the precipitation of tungsten carbide occurs progressively on tempering at higher temperatures and that this is the cause of the improvement in the stability of hardness upon tempering. Since tungsten forms either complex iron-tungsten carbides or the stable tungsten carbide WC, according to the heat treatment to which the steel is subjected,⁴ further experiments with tungsten steels were not performed.

Instead of pursuing the study of tungsten steels, a number of vanadium-iron-carbon alloys of varying composition were investigated.

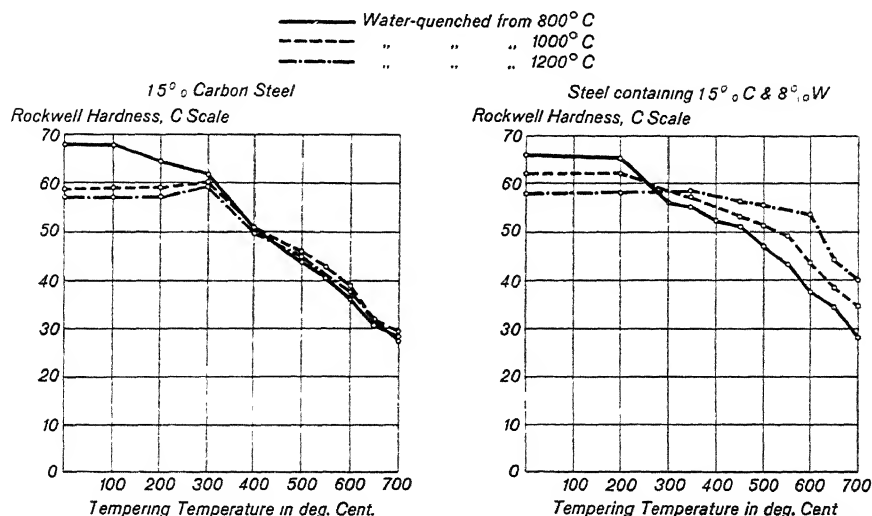


FIG. 4.—INCREASE OF STABILITY IN HARDNESS UPON TEMPERING IN TUNGSTEN STEEL, DUE TO INCREASE OF QUENCHING TEMPERATURE. ABSENCE OF THIS PHENOMENON IN A PLAIN CARBON STEEL OF OTHERWISE IDENTICAL COMPOSITION.

In view of the results of Maurer⁵ and of Vogel and Martin,⁶ it may be taken that only a single carbide of very low solubility occurs in the vanadium-iron-carbon alloys of industrial importance, so that complications due to the disintegration of metastable compounds need not be feared.

From the investigations of Hougardy,⁷ it appeared that vanadium carbide is practically insoluble and that therefore it will not dissolve in solid solution. He concluded that part of the total carbon is combined with vanadium and thus takes no part in the transformations occurring in the steel; however, the electrical resistance measurements carried out with the steels investigated by Hougardy show that vanadium carbide does actually pass into solution at higher temperatures, a fact that had

⁴ F. Pölguter and W. Zieler: *Stahl und Eisen* (1929) **49**, 522.

⁵ Maurer: *Stahl und Eisen* (1925) **45**, 1629.

⁶ Vogel and Martin: *Archiv f. d. Eisenhüttenwesen* (1930/31) **4**, 487.

⁷ Hougardy: *Archiv f. d. Eisenhüttenwesen* (1930/31) **4**, 497.

already been established by Maurer by means of physical measurements on vanadium-carbon steels.

A special influence exerted by vanadium carbide is evident from the unpublished investigations carried out in 1911 by F. Rittershausen, who found that vanadium steel exhibited different properties according to the temperatures from which it had been quenched. While no effect of the vanadium on the properties of steel could be detected when quenching from normal quenching temperatures, an increase in quenching temperature produced an important change in properties, as discussed below.

The range of steels investigated by the present authors is given in Table 3.

TABLE 3.—*Chemical Composition of Vanadium Steels Studied*

| Steel | | Composition, Per Cent | | | V |
|------------|--------------|-----------------------|------|------|------|
| | | C | Si | Mn | |
| 1st series | 0V0.4 | 0 01 | 0 01 | 0 02 | 0 35 |
| | 0V0.5 | 0 01 | 0 01 | 0 03 | 0 50 |
| | 0V0.9... .. | 0 01 | 0 01 | 0 03 | 0 90 |
| | 0V1.6... .. | 0 01 | 0 01 | 0 03 | 1 65 |
| | 0V2.2. | 0 01 | 0 01 | 0 02 | 2 22 |
| 2nd series | 5V0.. | 0 04 | 0 09 | 0 12 | |
| | 5V0.2 | 0 04 | 0 20 | 0 36 | 0 21 |
| | 5V0.3... .. | 0 04 | 0 15 | 0 32 | 0 31 |
| | 5V0.7. | 0 07 | 0 08 | 0 08 | 0 71 |
| | 5V0.9. | 0 05 | 0 01 | 0 04 | 0 86 |
| | 5V1.6. | 0 06 | 0 04 | 0 03 | 1 65 |
| | 5V3... | 0 07 | 0 04 | 0 10 | 2 97 |
| 3rd series | 15V0. | 0 12 | 0 36 | 0 45 | |
| | 15V1..... | 0 14 | 0 44 | 0 49 | 1 00 |
| | 15V2.5... .. | 0 14 | 0 42 | 0 41 | 2 49 |
| | 15V6 | 0 13 | 0 47 | 0 47 | 5 87 |
| 4th series | 35V0 | 0 39 | 0 33 | 0 59 | |
| | 35V0.2. | 0 36 | 0 31 | 0 46 | 0 21 |
| | 35V0.4. | 0 36 | 0 32 | 0 48 | 0 37 |
| | 35V0.6 | 0 43 | 0 31 | 0 24 | 0 64 |
| | 35V1.6. | 0 27 | 0 03 | 0 25 | 1 65 |
| | 35V3.7 | 0 36 | 0 04 | 0 21 | 3 69 |
| 5th series | 100V0. | 1 00 | 0 50 | 0 63 | |
| | 100V1.. | 0 94 | 0 45 | 0 51 | 1 10 |
| | 100V3... .. | 0 99 | 0 76 | 0 54 | 2 94 |
| | 100V6... .. | 1 01 | 0 64 | 0 53 | 6 00 |

The influence of vanadium and carbon on the Brinell hardness in the annealed and the normalized (air-cooled from 900° C.) conditions is shown

in Fig. 5. In both conditions there is a tendency for the hardness to decrease with increasing vanadium content. This, of course, is to be explained by the abstraction of carbon from the matrix owing to the formation of globular vanadium carbide.

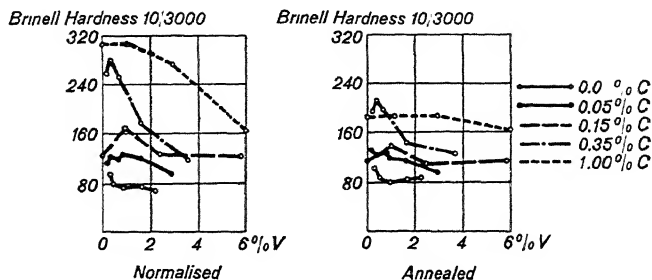


FIG. 5.—HARDNESS OF ANNEALED AND NORMALIZED CARBON-VANADIUM STEELS.

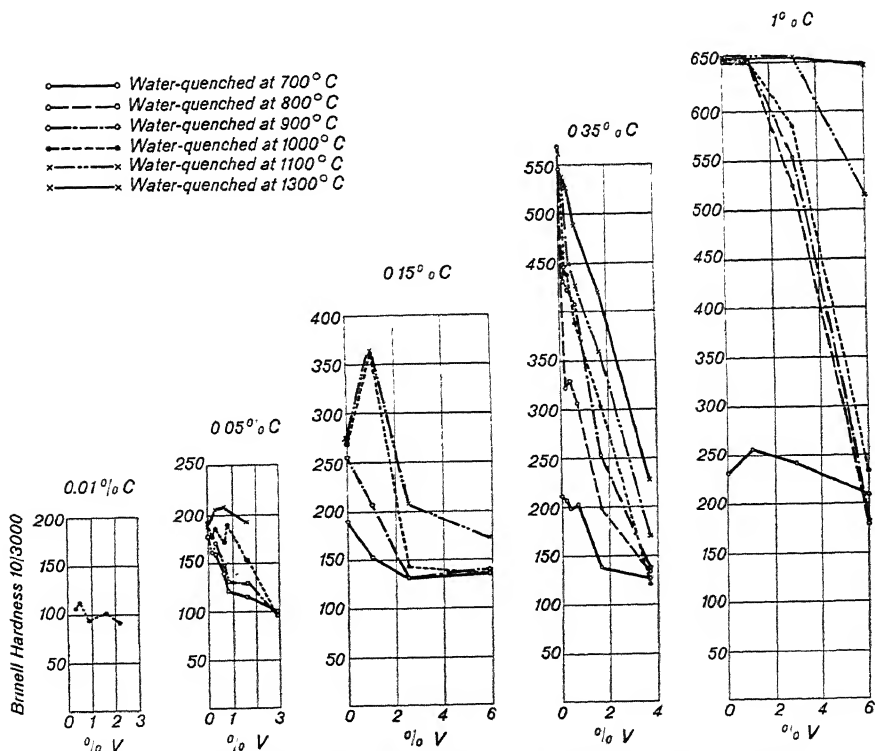


FIG. 6.—EFFECT OF VANADIUM ON QUENCH HARDNESS OF CARBON STEEL.

The variation in hardness brought about by quenching in water from different temperatures is given in Fig. 6. With low carbon contents, a decrease in hardening power is again shown for increasing vanadium content, while at the same time an increase in quenching temperature

results in a perceptible increase in hardness (contrary to the behavior of vanadium-free steel). The clearest results are those obtained with steels containing 1 per cent of carbon. At low quenching temperatures, the hardness decreased considerably with increasing vanadium content, while at temperatures in the range of 1250° to 1300° C. the same hardness was obtained as in plain carbon steels quenched from normal temperatures. Steels that lie outside the gamma region, owing to their high vanadium content, showed only a slight increase in hardness due to quenching.

It is interesting to note that alloys that are purely ferritic, owing to their low carbon content and high vanadium content, still showed an increase in hardness upon quenching of 50 to 60 Brinell numbers, a

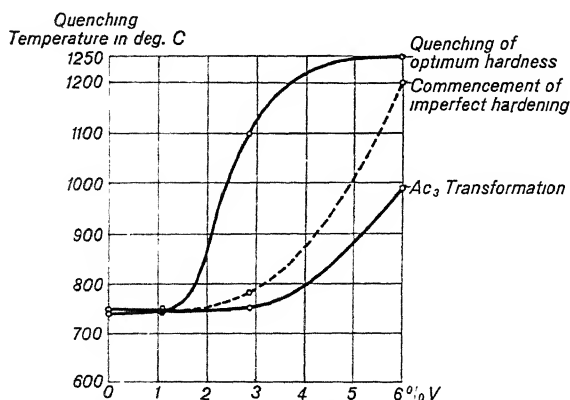


FIG. 7.—TEMPERATURE RANGES FOR OBTAINING VARIOUS DEGREES OF HARDNESS IN VANADIUM STEELS CONTAINING 1 PER CENT C, DETERMINED BY APPEARANCE OF FRACTURE AND BY HARDNESS TESTS.

phenomenon also observed by Maurer when experimenting with a steel that contained 1 per cent of carbon and 10 per cent of vanadium.

These quenching experiments should prove that it cannot be assured *a priori* that the vanadium carbide has no part in the process of hardening; on the contrary, with increasing temperature the vanadium carbide dissolves in solid solution, as shown by Maurer, and becomes an effective hardening agent. Only on this assumption can be the great hardness of steel containing 6 per cent of vanadium and 1 per cent of carbon be explained. The solution of the vanadium carbide in the austenite was confirmed by measurement of the specific electrical resistance.

Fig. 7 illustrates the exact hardening conditions for vanadium steels containing 1 per cent of carbon as a function of the quenching temperature and the position of the Ac₃ transformation. A noteworthy feature is the interval of temperature—increasing with the vanadium content—through which the vanadium steels must be heated above the Ac₃ point before the slightest hardening effect—even in incomplete form—sets in. In order to obtain optimum hardness, it is necessary to raise the temperature

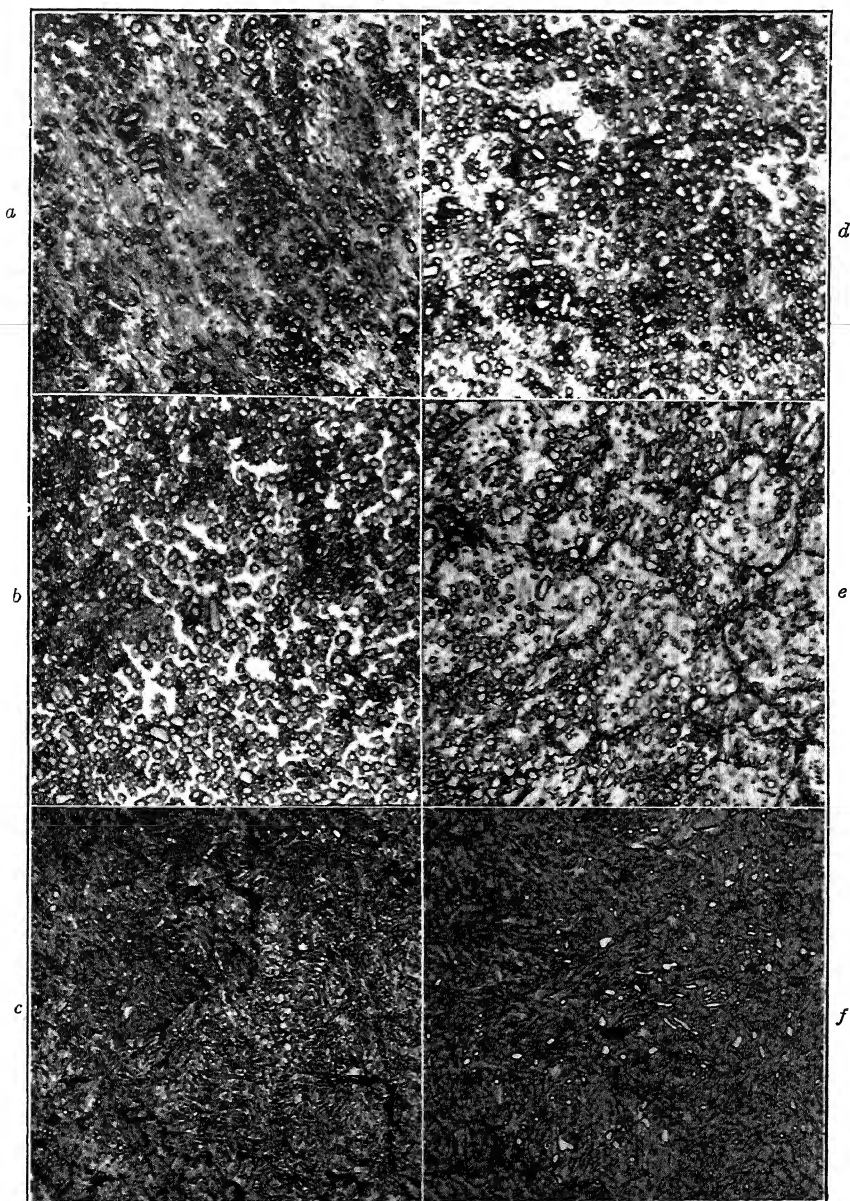


FIG. 8.—MICROSTRUCTURE OF QUENCHED VANADIUM STEELS CONTAINING 1 PER CENT CARBON.

- a. Steel containing 1 per cent carbon, water-quenched from 740° C.
- b. Steel containing 1 per cent carbon and 1 per cent vanadium, water-quenched from 900° C.
- c. Steel containing 1 per cent carbon and 3 per cent vanadium, water-quenched from 1100° C.
- d, e and f. Steel containing 1 per cent carbon and 6 per cent vanadium.
- d. Water-quenched from 900° C.
- e. Water-quenched from 1100° C.
- f. Water-quenched from 1300° C.

Etched with 3 per cent nitric acid.

even further. Microscopic examination shows that the region of imperfect hardening is characterized by the presence of a considerable quantity of undissolved vanadium carbide, which exerts an intensifying influence on the tendency to transformation during the hardening process and thus acts as nuclei in facilitating the formation of troostite. At temperatures up to 900°C ., and even up to 1100°C ., depending upon the vanadium content, the grain boundaries exhibit remnants of troostite, the greater part of which is in direct connection with accumulations of carbide (Fig. 8). The photographs of the steel containing 6 per cent vanadium

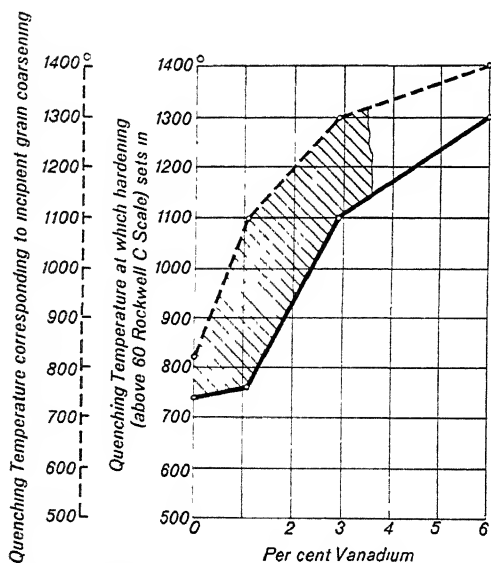


FIG. 9.—QUENCHING TEMPERATURE RANGE FOR VANADIUM STEELS CONTAINING 1 PER CENT CARBON.

and 1 per cent carbon clearly show the dissolution of the vanadium carbide with increasing temperature. It will also be noted that the structure assumes a hardenitic appearance, whereas plain carbon steels form a coarse acicular martensite upon quenching from 900°C . Vanadium steel quenched from high temperatures possesses a structure closely resembling that of high-speed tool steel.

In vanadium steels, as in tungsten steel, the embedded carbides also render the steel less sensitive to overheating; in other words, the temperature range available for successful hardening is increased (area in Fig. 9). This is shown very clearly in steels low in vanadium, where iron carbide is present in sufficient quantity to produce full hardness within a fairly narrow temperature range above A_{c3} . In the case of high vanadium contents optimum hardness is not obtained until larger quantities of vanadium carbide have gone into solution; accordingly

the range of temperatures from the best hardening temperature to the overheating temperature is not larger than for plain carbon steels.

As a consequence of the abstraction of carbon from the matrix through the formation of vanadium carbide and of the inoculating effect of the vanadium carbide upon the transformation, vanadium has the further effect of reducing the depth of hardening obtainable in quenching from normal temperatures. This is proved by a comparison of a steel containing 1 per cent carbon and 1 per cent vanadium with a steel containing 1 per cent carbon but no vanadium. This result is in agreement with the findings of others.⁵

Since plain carbon steels and vanadium steels harden throughout a cross-section of 30 mm. on a side, and since increase in quenching temperature increases the depth of hardening, it is necessary in studying the

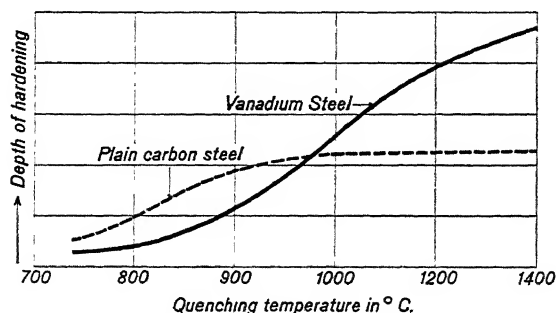


FIG. 10.—SCHEMATIC REPRESENTATION OF DEEP-HARDENING CAPACITY OF STEEL CONTAINING 1 PER CENT CARBON AND 1 PER CENT VANADIUM, AS COMPARED WITH PLAIN CARBON STEEL.

effect of high quenching temperatures in vanadium steels to use a larger section; a section of 80 mm. on a side was adopted and found satisfactory. Quenching temperatures from 1000° C. upwards increase the capacity of vanadium steel for deep hardening, yet despite these high temperatures vanadium steel quenched from temperatures up to 1100° C. showed an extremely fine-grained fracture. This influence of vanadium is represented schematically in Fig. 10. These observations on vanadium-bearing steels thus confirm the observations on tungsten steels, and justify the conclusion that in steels containing such special carbides an increase in hardening power and a material change in the critical rate of cooling in comparison with plain carbon steels are afforded, entirely because of the solution of the special carbides.

It is still necessary to inquire how the solution of vanadium carbide at high quenching temperatures affects the stability of hardness on tempering. When quenched from below A_{c_3} and even from 800° C., the tempering curves of vanadium steels do not differ materially from those of plain

⁵ F. Schilling: *Kruppsche Monatshefte* (1923) 4, 123; *Stahl und Eisen* (1923) 43, 1048.

carbon steels. But vanadium steels quenched from 900° C. and tempered at about 600° show a slight anomaly in the course of the hardness-temperature curves (Fig. 11), which becomes quite conspicuous when the steel is quenched from 1000° C. (Fig. 12).

In order to make sure that the increase in hardness upon tempering at 600° C. could not be ascribed to a specific effect of the vanadium itself, a series of specimens practically free from carbon was included in the investigation. As expected, these specimens showed that the hardness is in no way dependent upon the quenching or tempering temperatures. But with as low a carbon content as 0.05 per cent an increase in hardness was noted between 550° and 650° C. tempering temperature in steels that,

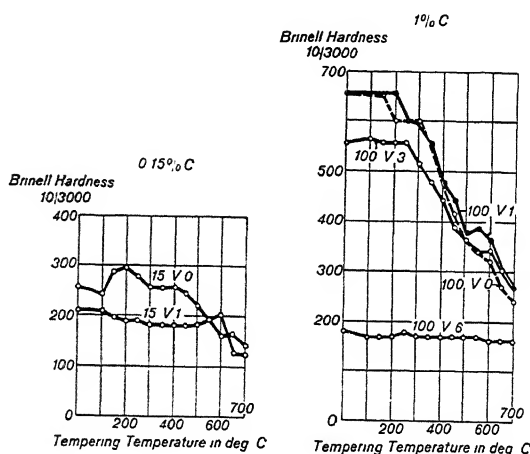


FIG. 11.—VARIATION OF HARDNESS PRODUCED BY TEMPERING VANADIUM STEELS PREVIOUSLY WATER-QUENCHED FROM 900° C.

because of the vanadium and carbon content, lie within the gamma region. This occurs also for steels containing 0.15, 0.35 and 1 per cent carbon. In low-carbon steels (0.05 and 0.15 per cent), these phenomena persist in approximately the same degree at quenching temperatures up to 1300° C.

High-vanadium steels with a higher carbon content assume a marked hardness only at quenching temperatures from 1100° C. upward. Consequently, the tempering phenomena also make their appearance only after quenching from these high temperatures. The stability of hardness upon tempering increases with the quenching temperature and the proportion of dissolved vanadium carbide (Fig. 13). This effect of the vanadium makes itself felt even with very low vanadium contents, such as are sometimes encountered in eutectoid tool steels (Table 4). At temperatures up to 400° C. there is practically no difference in hardness between plain carbon steels and vanadium steels. Even at higher tempering temperatures vanadium steels quenched from 800° C. scarcely

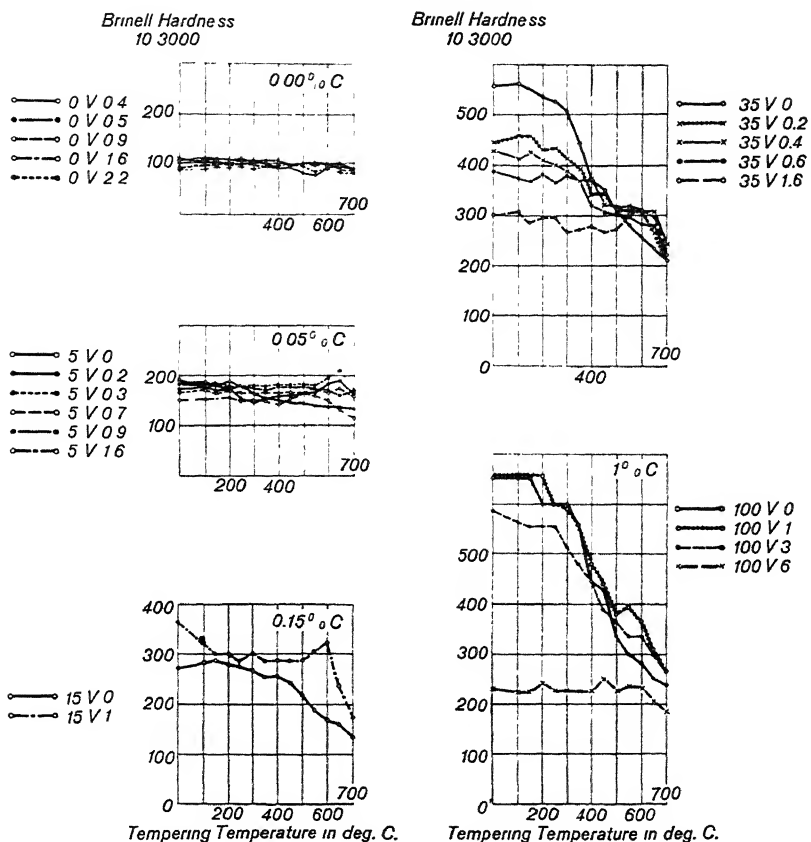


FIG. 12.—VARIATION OF HARDNESS PRODUCED BY TEMPERING VANADIUM STEELS PREVIOUSLY WATER-QUENCHED FROM 1000° C.

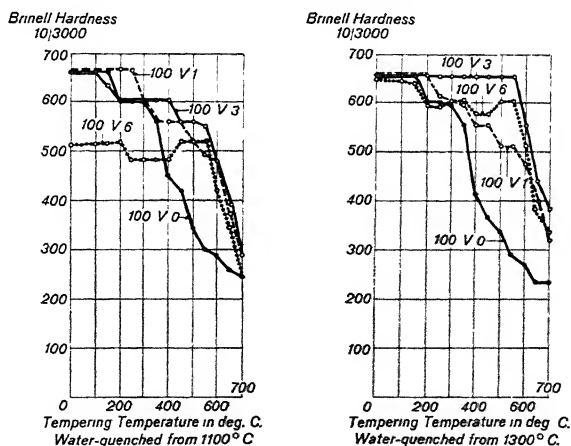


FIG. 13.—INCREASE OF STABILITY IN HARDNESS UPON TEMPERING IN VANADIUM STEELS CONTAINING 1 PER CENT CARBON, DUE TO INCREASE IN QUENCHING TEMPERATURE

differ from carbon steels. Only with highest quenching temperatures will steels tempered at 550° to 650° C. show an increase in hardness corresponding to that revealed by the other investigations. As there was reason to surmise that the time factor is of importance for the solution of the carbides, the time of retention at the quenching temperature was increased up to 10 hr. without any change in results. Therefore it must be concluded that heating to quenching temperature for the normal time, about 10 minutes, suffices to induce a state of equilibrium in the solution of the vanadium carbide.

Since the tempering effect observed in vanadium steels might be attributed not to a precipitation of the vanadium carbide but to a trans-

TABLE 4.—*Increase of Stability in Hardness in 1 Per Cent Carbon Steel upon Tempering, Due to Increase of Quenching Temperature and Slight Addition of Vanadium.*

| Steel | Treatment for hardening | Rockwell-C Hardness after quenching | Rockwell-C Hardness after tempering at | | | | | 700° Brinell 10/3000 |
|-----------|---------------------------------|--|---|-------|-------|-------|------------|----------------------------|
| | | | 300° | 400° | 500° | 600° | Rockwell C | |
| 100 V 0 | Water-quenched from 800° C. | 68–70 | 54–55 | 47–48 | 35–37 | 27–28 | | 172 |
| | Water-quenched from 900° C. | 68–69 | 53–54 | 47–48 | 35–36 | 26–28 | | 170 |
| | Water-quenched from 1000° C. | 68–69 | 53 | 46–47 | 35–36 | 27–28 | | 175 |
| 100 V 0.1 | Water-quenched from 800° C. | 69–70 | 55–54 | 46–47 | 37–38 | 29–30 | | 190 |
| | Water-quenched from 900° C. | 67–69 | 54 | 45–46 | 39–40 | 33–34 | | 209 |
| | Water-quenched from 1000° C. | 67–69 | 54 | 46–47 | 39–40 | 32–34 | | 211 |

formation of residual austenite, such as is known to occur in high-speed tool steel when tempered at about 600° C., all the steels studied were subjected to measurement of magnetic saturation, for the purpose of determining their austenite content (Fig. 14). The steels were quenched from temperatures at which the precipitation effect was already clearly noticeable, and afterwards tempered at temperatures varying from 100° to 600° C. The saturation measurements were carried out on cooled specimens in a field of 10,000 gauss, in comparison with the same steels annealed at 750° C. for 3 hr. and cooled in the furnace.

The amount of residual austenite in the vanadium-bearing steels is lower than in plain carbon steels, owing to the enhanced tendency towards transformation induced by the numerous carbide particles still present at the quenching temperatures. The series of low-carbon specimens

shows practically no residual austenite, though a distinct increase in hardness sets in on tempering. The essential point is that the disintegration of the residual austenite occurs at the same temperatures as for plain carbon steels; viz., about 300° C. From this temperature on, all steels possess the complete saturation of the annealed state. A transformation of residual austenite into martensite therefore cannot account for the secondary increase in hardness observed in vanadium steels upon tempering at about 600° C. As mentioned above, such a possibility is also

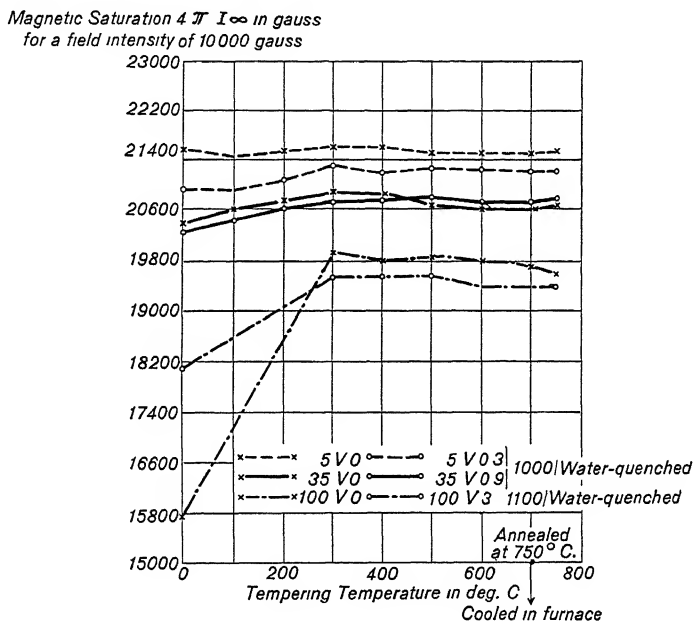


FIG. 14.—VARIATION OF MAGNETIC SATURATION.

prohibited by the fact that a vanadium steel after having been tempered for one or more times, for example at 550° C., exhibiting thereupon the secondary increase in hardness, can be subsequently tempered at 600° C. producing a final hardness identical with that produced by the first tempering at 600° C. Any martensite newly formed from residual austenite would suffer a tempering effect under such circumstances; i.e., a softening.

It might still be objected that vanadium steels on being quenched retain a certain amount of residual austenite, which during the tempering process precipitates carbides that increase the hardness or enhance the stability of hardness on tempering, without changing the residual austenite (impoverished in carbon) into martensite. This, of course, would not produce an increase in the value of magnetic saturation. However, the formation of an austenite of a stability which when annealed at 750° C. would not be changed into alpha iron is inconsistent with the

general behavior of vanadium steels in hardening. There is nothing whatever to show that vanadium has a stabilizing effect on the gamma solid solution. Such a stabilization of austenite is particularly inconceivable in the case of the low-carbon alloys that possess very slight hardening power. It can further be shown that the degree of saturation

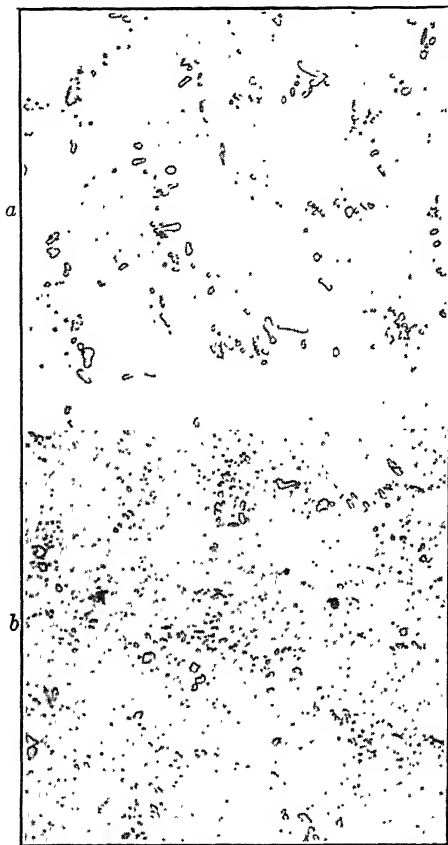


FIG. 15.—PRECIPITATION OF CARBIDE, VISIBLE UNDER MICROSCOPE, IN STEEL CONTAINING 1 PER CENT CARBON AND 3 PER CENT VANADIUM.

actually found in the steels investigated agrees so closely with the saturation calculated, when allowance is made for the reduction of saturation due to the non-magnetic alloying elements, that an appreciable amount of austenite cannot possibly be present. Attention is further drawn to the fact that all precipitations known in austenite and austenitic steels, capable of producing a perceptible hardening effect, occur at much higher temperatures (700° to 800° C.).⁹ Finally, it would be necessary to assume that vanadium steels form two different types of residual austenite, one of which changes into martensite in the usual way at tempering temperatures up to 300° C. and another that possesses extraordinary stability. All this evidence indicates that the possibility of a transformation of residual austenite on tempering can safely be left out of consideration. The increase in hardness that occurs in steels containing vanadium carbide when tempered at 600° C. must there-

fore be ascribed to a change in the nature of the martensite or the alpha iron, respectively.

Metallographic observations, which demonstrated the progressive solution of the vanadium carbide at higher temperatures, also revealed the precipitation of an extremely finely dispersed constituent on tem-

⁹ B. Strauss, H. Schottky and J. Hinnüber: *Ztsch. f. anorg. u. allg. Chem.* (1930) 188, 309.

A. Bennek and P. Schafmeister: *Archiv f. d. Eisenhüttenwesen* (1931/32) 5, 615.

W. Koster: *Archiv f. d. Eisenhüttenwesen* (1932/33) 6, 17.

pering. It is true that precipitation can only be observed metallographically in the case of prolonged tempering at about $750^{\circ}\text{C}.$; in other words, at a temperature from 100° to $150^{\circ}\text{C}.$ higher than the temperature of maximum increase in hardness. Fig. 15 shows two unetched sections of the specimen containing 1 per cent carbon and 3 per cent vanadium, in the quenched state and after having been tempered at $750^{\circ}\text{C}.$, respec-

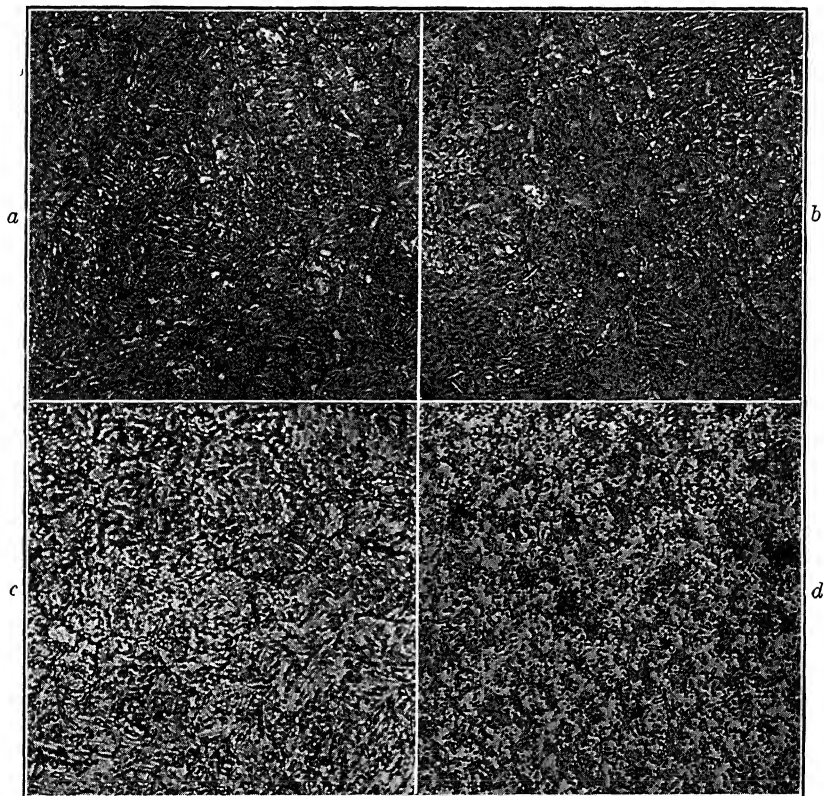


FIG. 16.—MICROSTRUCTURE OF STEEL CONTAINING 3 PER CENT VANADIUM AND 1 PER CENT CARBON, IN TEMPERED CONDITION.

- a. Water-quenched from $100^{\circ}\text{C}.$, tempered 1 hr. at $500^{\circ}\text{C}.$
 - b. Water-quenched from $1100^{\circ}\text{C}.$, tempered 1 hr. at $600^{\circ}\text{C}.$
 - c. Water-quenched from $1100^{\circ}\text{C}.$, tempered 1 hr. at $750^{\circ}\text{C}.$
 - d. Water-quenched from $1100^{\circ}\text{C}.$, tempered 3 hr. at $750^{\circ}\text{C}.$
- Etched with 3 per cent nitric acid.

tively. The retarded precipitation of the vanadium carbide also delays the disintegration of the martensite structure, as apparent in Fig. 16.

That the phenomena on tempering are due to a kind of precipitation-hardening is also proved by the hardness-tempering time curves reproduced in Fig. 17. Whereas at $500^{\circ}\text{C}.$ tempering temperature, the hardness increases up to 100 hr. exposure to that temperature, it decreases after 100 hr. exposure to a tempering temperature of $600^{\circ}\text{C}.$, and more quickly if the tempering temperature be increased to $650^{\circ}\text{C}.$ In the

steel of very low carbon content, precipitation-hardening sets in in the course of the very first hour.

The whole of the investigations described so far would seem to prove beyond dispute that in the hardening of vanadium-carbon steels the vanadium carbide that dissolved at higher temperatures does not, in spite of the gamma-alpha transformation having occurred, precipitate from the alpha solid solution at temperatures below 500° to 600° C., and

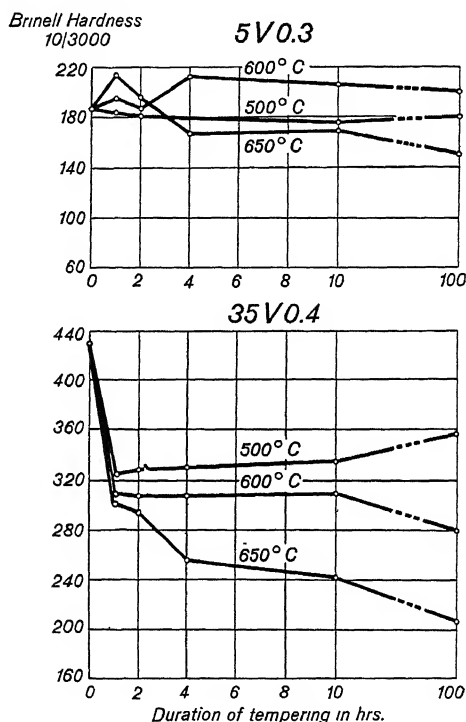


FIG. 17.—INFLUENCE OF DURATION OF TEMPERING ON HARDNESS OF LOW-VANADIUM STEELS.

that when it does precipitate at proper tempering temperatures it causes an increase in hardness, which imparts to the steel the property of resistance to tempering.

The observed stability of hardness upon tempering due to the presence of vanadium, and its dependence upon variation in the quenching temperature (which must be regarded as a specific effect of the vanadium carbide) must also be reflected in the mechanical properties of the steel. The stability of the high tensile strength of vanadium-bearing constructional steels on tempering has been mentioned by Putz,¹⁰ Hohage and Grutzner,¹¹ and others.

¹⁰ Putz: *Metallurgie* (1906) **3**, 635.

¹¹ Hohage and Grutzner: *Stahl und Eisen* (1925) **45**, 1126.

Since the conception that the special effects exerted by vanadium are caused by a precipitation of vanadium carbide is entirely new, it appeared advisable to perform additional experiments upon these steels. Because of the low vanadium and carbon contents present in constructional steels, these investigations were mainly limited to steels containing, respectively, 0.05 and 0.35 per cent carbon, with vanadium contents up to 0.4 per cent. Since earlier researches, dealing in particular with copper and titanium, had shown that a certain amount of precipitation-hardening often increases the yield point rather than the tensile strength, the ratio of the yield point to tensile strength was taken as a measure of the amount of precipitation-hardening occurring. Fig. 18 clearly shows the influence of precipitation within the temperature range from 500° to 600° C. Whereas the vanadium-free steels exhibit the usual changes in mechanical properties on tempering, the influence of the carbide precipitation in the vanadium-bearing steels is clearly discernible. In the case of the 5 V 0.2 steel the yield point curve clearly indicates a rise above 500° C. (after an initial decrease between 300° and 500° C.), and the tensile-strength curve also shows an increase in this temperature range, though not so pronounced; but the yield ratio shows a pronounced increase. The effect is still more marked in the 5 V 0.3 steel.

In the case of the 35 V 0.2 and 35 V 0.4 steels, which are richer in carbon, the loss in tensile strength at 300° to 500° C., due to the coagula-

TABLE 5.—*Effect of Duration of Tempering on Tensile Properties of Vanadium Steels Tempered at 600° C.*

| Steel | Heat Treatment | Yield Point, Kg. per Sq. Mm. | Tensile Strength, Kg. per Sq. Mm. | Yield Ratio, Per Cent | Elongation, ($l = 5d$), Per Cent | Reduction in Area, Per Cent |
|----------|--|------------------------------------|---|--------------------------|--|-----------------------------------|
| 5 V 0.3 | Oil-quenched from 950° and tempered 1 hr. at 600° C. 8 hr. at 600° C... | | | | | |
| | | 43 | 47.7 | 90.3 | 29.0 | 79 |
| | | 48 | 57.1 | 84.4 | 26.4 | 78 |
| 35 V 0.4 | Oil-quenched from 950° and tempered 1 hr. at 600° C. 8 hr. at 600° C... | | | | | |
| | | 91 | 101.4 | 89.8 | 18.4 | 57 |
| | | 86 | 99.9 | 86.1 | 18.2 | 55 |

tion of the iron carbide, is more pronounced, in accordance with the greater proportion of this constituent. Nevertheless, here again the influence of vanadium carbide precipitation, particularly on the yield point and on the yield ratio, is clearly marked. With precipitation beginning at 500° C., there occurs a decrease in ductility, as may be seen

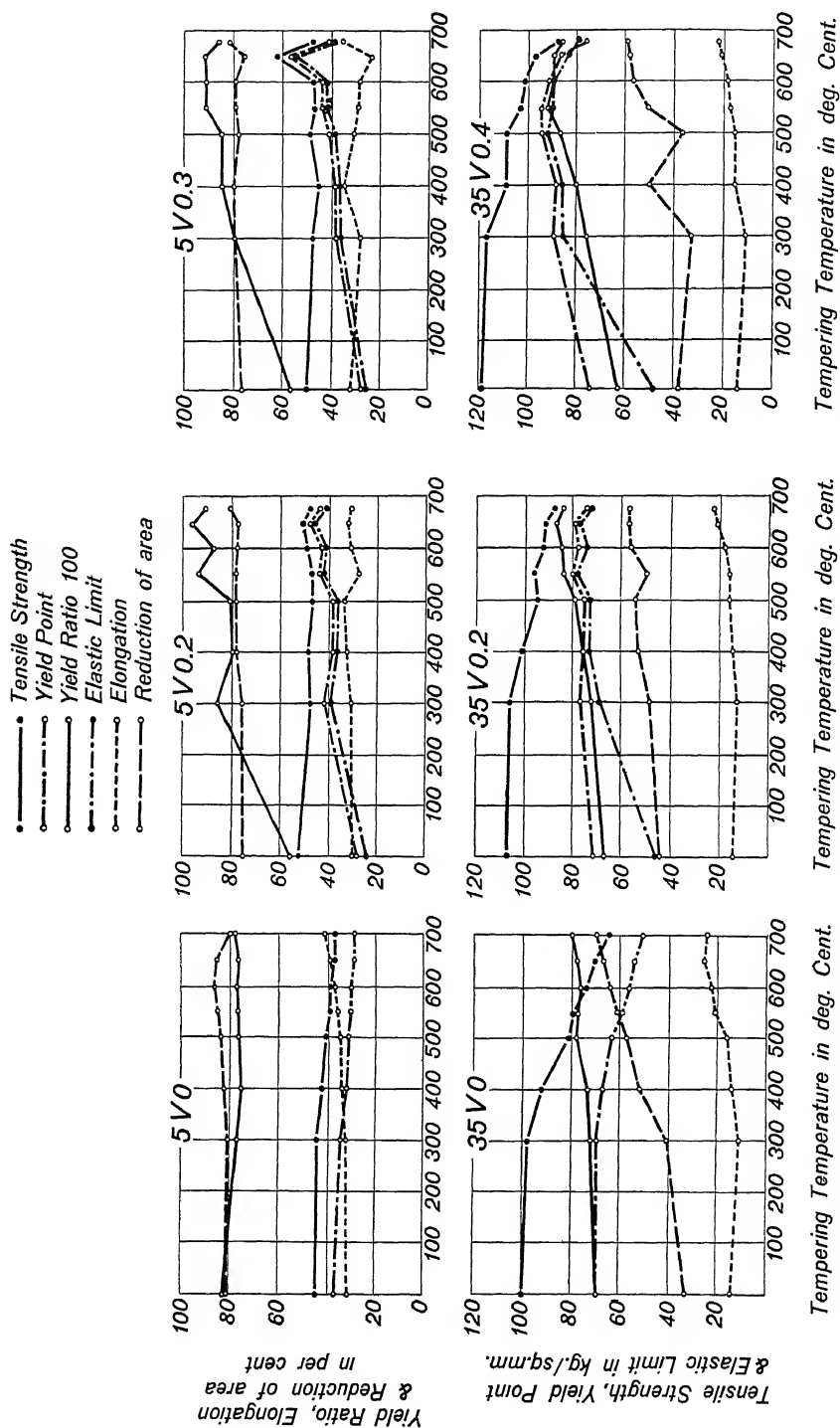


FIG. 18.—VARIATION IN TENSILE PROPERTIES OF LOW-VANADIUM STEELS DUE TO VARIATION IN TEMPERING TEMPERATURE.

most clearly in the 35 V 0.4 steel. The change in tensile properties following an increase in tempering time at the same temperature is in agreement with the isothermals in Fig. 17.

Table 5 gives the different results obtained by tempering the 5 V 0.3 and 5 V 0.4 steels for periods of 1 and 8 hr. Whereas in the case of the steel with the higher carbon content the tensile strength and yield point have already passed through their maximum after the lapse of 8 hr., the low-carbon steel does not show this behavior, a fact that is in accord with the hardness results. The impact strength (as measured by means of the Mesnager specimen) of the same two steels after different heat treatment is given in Table 6. The figures can be regarded as satis-

TABLE 6.—*Impact Strength of Tempered Vanadium Steels*
KG-M. PER SQ. CM. AFTER OIL-QUENCHING FROM 950° C. FOLLOWED BY TEMPERING

| | 1 Hr. at 500° | 1 Hr. at 600° | 1 Hr. at 650° | 8 Hr. at 600° |
|--------------------|---------------|---------------|---------------|---------------|
| 5 V 0.3 | 30 | 30 | 29 | 22 6 |
| 35 V 0.4 | 10.2 | 7.9 | 12.1 | 8.5 |

Mesnager specimen 10 × 10 × 55 mm., area of fracture 10 × 8 mm.

factory, although the values usually associated with high-grade constructional steels of the same tensile strength were not attained in the

TABLE 7.—*Influence of Sectional Area on Variation of Tensile Properties Induced by Precipitation of Carbide in Vanadium Steel*

STEEL 35 V 0.4 OIL-QUENCHED FROM 1000° AND TEMPERED 100 HR. AT 500°

| Diameter, Mm. | Reduction by Forging | Position of Test Piece | Yield Point, Kg. per Sq. Mm. | Tensile Strength, Kg. per Sq. Mm. | Yield Ratio, Per Cent | Elongation, ($l = 5d$), Per Cent | Reduction, of Area, Per Cent | Impact Strength, Kg.-m. per Sq. Cm. ($10 \times 10 \times 55$ Mm.) |
|---------------|----------------------|------------------------|------------------------------|-----------------------------------|-----------------------|------------------------------------|------------------------------|---|
| 20 | 49 fold | | 104 | 112 | 93 0 | 12 7 | 46 | 4.0 |
| 40 | 12 2 fold | Outside | 92 | 105.9 | 87 0 | 14 7 | 50 | 2.3 |
| | | Inside | 90 | 104 8 | 91 0 | 16 | 49 | 1.7 |
| 60 | 5.5 fold | Outside | 89 | 104 3 | 85 3 | 14 8 | 45 | 2.2 |
| | | Inside | 85 | 102 7 | 82 8 | 13 4 | 40 | 1.5 |

case of the 35 V 0.4 steel. It is, of course, well known that precipitation phenomena are generally accompanied by a decrease in impact strength. This is true also of the precipitation of vanadium carbide, as conclusively proved by the further experiments on the 35 V 0.4 steel (with specimens of various cross-sectional area, with a view to ascertaining at least within certain limits the influence of cross-sectional area).

Table 7 sets forth the results obtained with specimens of 20, 40 and 60 mm. dia. These specimens were oil-quenched from 1000° C. and

TABLE 8.—Effect of Addition of Vanadium in Alloy Steels. Increasing Resistance to Tempering with Increasing Quenching Temperature.
(From researches by Rittershausen)

| | Heat Treatment | | Yield Point/ kg./sq.mm. | Tensile Strength/ kg./sq.mm. | Elongation (l = 5 d)/% | Reduction of area/% | Impact Strength/ kg.m./sq.cm. |
|--|------------------|---------------------|----------------------------|---------------------------------|---------------------------|------------------------|----------------------------------|
| | Quenched from | Quenching Medium | | | | | |
| Chromium Steel containing C 0.29 Si 0.14 Mn 0.15 Cr 1 per cent | 850° | Oil | 44 | 70 | 25.2 | 66 | 23.8 |
| | 950° | Oil | 46 | 70 | 18.3 | 64 | 18.7 |
| Chromium-vanadium Steel containing C 0.26 Si 0.10 Mn 0.13 Cr 0.96 V 0.27 per cent | 850° | Oil | 40 | 63.7 | 24.8 | 69 | 15.3 |
| | 950° | Oil | 78 | 100.8 | 16.5 | 59 | 8.0 |
| Chromium-nickel Steel containing C 0.31 Si 0.06 Mn 0.29 Ni 4.10 Cr 1.17 per cent | 800° | Water | 70 | 87 | 23.0 | 68 | 24.4 |
| | 900° | Water | 68 | 90 | 23.8 | 66 | 21.2 |
| | 950° | Water | 74 | 91 | 24.6 | 66 | 21.5 |
| | 1000° | Water | 72 | 92 | 20.7 | 66 | 20.4 |
| Chromium-nickel-Vanadium Steel containing C 0.29 Si 0.24 Mn 0.26 Ni 4.34 Cr 1.52 V 0.48 per cent | 800° | Water | 74 | 86 | 20.4 | 66 | 22.4 |
| | 900° | Water | 104 | 117 | 17.5 | 59 | 10.2 |
| | 950° | Water | 102 | 124 | 16.3 | 53 | 4.1 |
| | 1000° | Water | 118 | 134 | 12.0 | 41 | 3.0 |

*) With subsequent oil-cooling

tempered at 500° C. for 100 hr., in accordance with the maximum effect indicated by the isothermals in Fig. 17. As appears from Table 7, the yield ratio for the 60-mm. dia. section is slightly lower than for the smaller sections. The notched-bar impact value is very low. For plain vanadium-carbon steels, with cross-sections of 60 mm. dia. and upwards, it would be necessary to resort at least to water-quenching in order to secure a uniform effect throughout the cross-section.

The theories evolved in connection with plain carbon-vanadium steels in explanation of the effect of the vanadium carbide are directly applicable to complex constructional steels. This is apparent from the results obtained in 1911 by F. Rittershausen, which led the authors to undertake the present work. Some typical examples of Rittershausen's results are given in Table 8.

The chromium steels as well as the chromium-nickel steels plainly show that when quenched from normal temperatures the vanadium content exerts no effect upon the mechanical properties; on the contrary, owing to some of the carbon combining with the vanadium, there is a tendency for the vanadium-bearing steels to be somewhat softer. When higher quenching temperatures are employed, the vanadium-free steel remains on the whole unaffected, whereas the vanadium-bearing steels exhibit the marked effect of the vanadium in increasing the tensile strength, yield point, etc., upon tempering. At the same time, the impact values fall off considerably, owing to the precipitation of vanadium carbide.

In chromium-molybdenum steels, which of themselves show considerable resistance to tempering, maintaining high tensile strength and yield point, etc., on tempering at high temperatures, an addition of vanadium coupled with an increase in quenching temperature produces a similar improvement in the mechanical properties (Fig. 19). When such a steel is quenched from a lower temperature, the influence of the molybdenum alone makes itself felt on tempering at 550° C. Only with increasing quenching temperature does the effect of the vanadium appear also on tempering at 600° C.

From the above we may conclude that an addition of vanadium to constructional steels will produce no effect on the mechanical properties unless the quenching temperature is raised so as to utilize the influence of the vanadium carbide. The only effect of an addition of vanadium to constructional steels quenched from normal temperatures is to produce a fine grain, owing to the retardation in grain growth in the austenite by carbide particles. The finer grain of vanadium steels causes a higher ratio of yield point to tensile strength. The effectiveness of vanadium as a deoxidizer is well known and need not be discussed here.

Particular interest is attached to a study of vanadium steels treated in various ways, with respect to their strength at elevated temperatures.

P. Prömper and E. Pohl¹² some years ago called attention to the maintenance of strength at elevated temperatures exhibited by vanadium-alloyed mild steel, and proposed the use of such material for boiler construction. It has been known for some time that this improvement

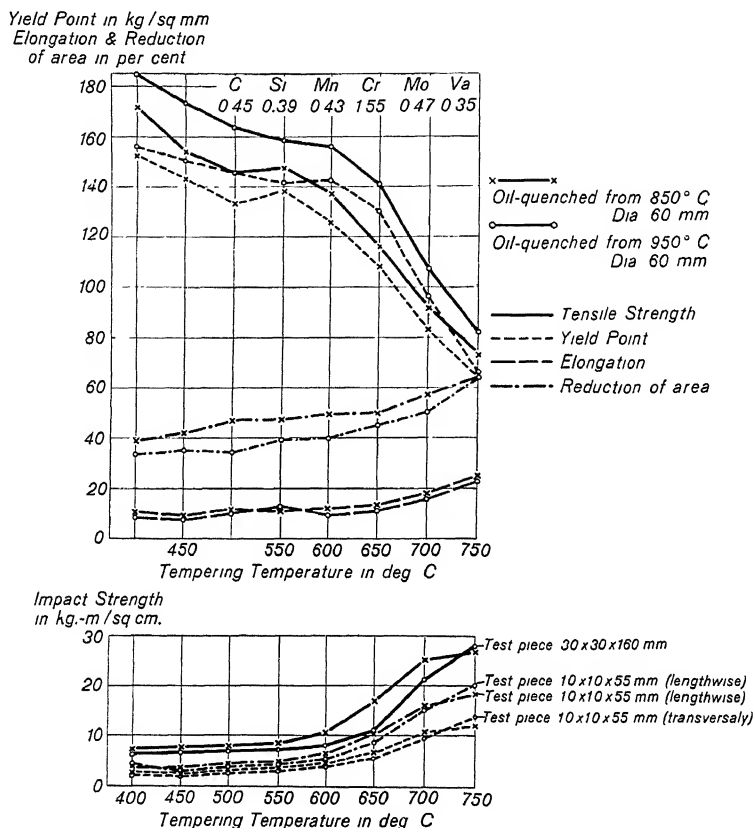


FIG. 19.—VARIATION OF TENSILE PROPERTIES OF CR-MO-V STEEL WITH VARYING TEMPERING TEMPERATURES.

in the mechanical properties cannot always be obtained. It is reasonable therefore to suspect that increased retention of strength at elevated temperatures can be obtained only under certain definite conditions induced by heat treatment, where the precipitation of the vanadium carbide plays a part.

Fig. 20 shows the tensile values of variously treated low-carbon vanadium steels tested at 500° and 600° C. The steel that has not been tempered at all, and that which has been tempered at 600° C., exhibit higher tensile values under the temperature conditions of the test. Of the two, the one that had not been tempered is bound to exhibit the

¹² P. Prömper and E. Pohl: *Archiv f. d. Eisenhüttenwesen* (1927/28) **1**, 785.

more pronounced effect during the tensile test of 20-min. duration, since the precipitation in this case can start only during the tensile test itself. The steel that had been tempered at 700° C. shows at elevated temperatures tensile properties that do not differ essentially from those found with plain carbon steel, particularly as regards the yield point. Thus it is clear that the tensile strength and the yield point at elevated temperatures are raised by the precipitation of the special carbide. Evidently this will hold equally well for all other steels that

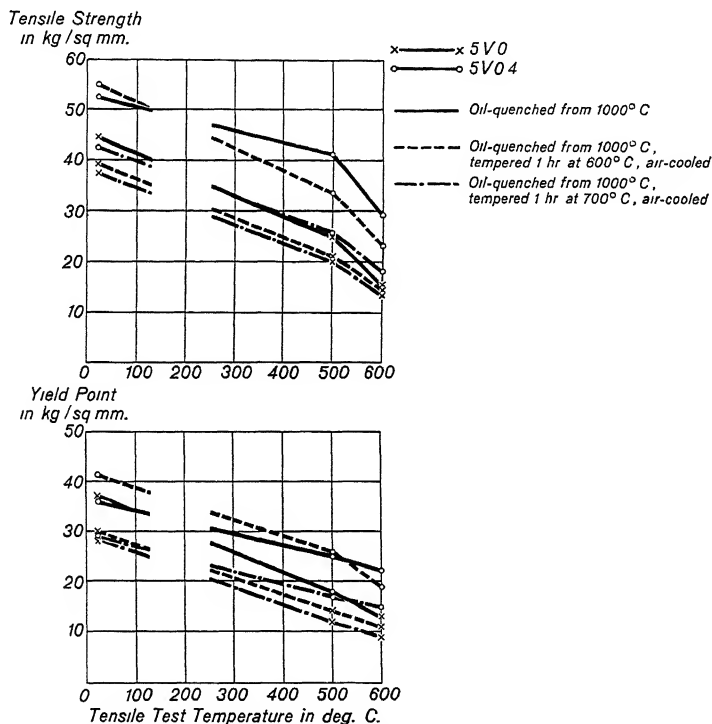


FIG. 20.—INFLUENCE OF VANADIUM ON TENSILE PROPERTIES AT HIGH TEMPERATURES OF VARIOUSLY TREATED LOW-CARBON STEELS.

under similar conditions will form special carbides. In considering the tensile properties of steels of this type at elevated temperatures it will therefore always be necessary to take into account the condition in which they are examined; the as-rolled state, in particular, must be regarded as an indeterminate state. Considering, however, the fact that at 500° C. the precipitation of vanadium carbide does not progress far enough in 100 hr. for a decrease in hardness to occur, it is quite legitimate to claim a lasting increase in high-temperature hardness and strength of vanadium-bearing steels upon suitable treatment.

One of the most important requirements for cutting steels, especially high-speed steel, is that of red-hardness. Vanadium steels of rather

high carbon content, possessing characteristics similar to those of tool steel, have therefore been studied with a view to determining their cutting efficiency under definite conditions.

Fig. 21 illustrates the influence of vanadium on the cutting life of tools worked at two different cutting speeds. Although the 6 per cent vanadium steel does not have the long tool life of the best grades of high-speed steel, the marked effect of vanadium with respect to tool life is nevertheless unmistakable. It must be borne in mind that the vanadium steels studied from this point of view all possessed identical carbon contents (1 per cent); it would be illogical to assume *a priori* that this

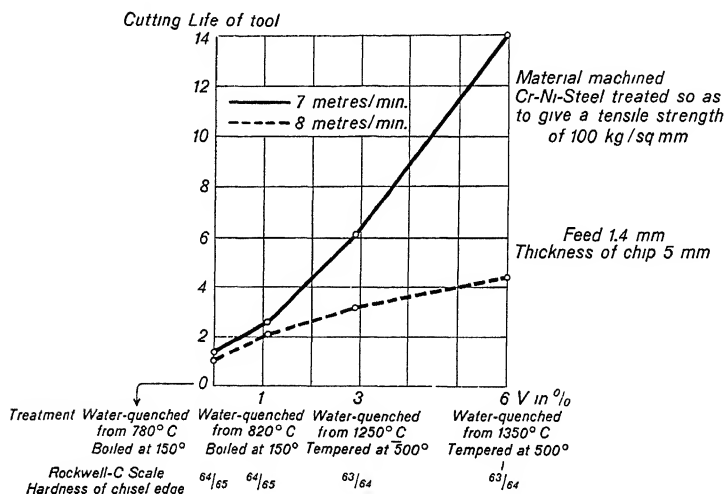


FIG. 21.—EFFECT OF VANADIUM ON CUTTING EFFICIENCY OF PLAIN CARBON STEEL.

carbon content and no other represents the optimum percentage for securing maximum tool performance in combination with all of the various vanadium contents examined. However, the results found are sufficient to demonstrate clearly the influence of vanadium in high-speed steel.

The same laws that govern the influence of vanadium in steels hold good for the other elements that form special carbides. Earlier in this paper it was shown that the behavior of tungsten steels corresponds to that of vanadium steels. Similar phenomena occur in chromium steels. With increasing quenching temperature, steels with rather high contents of chromium and carbon undergo a change in the critical rate of cooling, owing to the progressive solution of the chromium carbides in the solid solution, assuming the character of an oil-hardening or air-hardening steel. At the same time the stability of hardness upon tempering is also increased by the chromium carbides.

According to recent investigations by C. Küttner and W. Tofaute, a 15 per cent chromium steel heated to 500° C. precipitates a stable

chromium carbide. It is a well-known fact that chromium steels at 500° C. also exhibit a stability in hardness upon tempering and even an increase in hardness upon tempering like that found in vanadium steels. Furthermore, this behavior furnishes information on the corrosion resistance of these steels. As is well known, steels containing from 13 to 15 per cent of chromium with 0.5 per cent of carbon show good anti-corrosive properties in the quenched state; but after being tempered at from 500° to 650° C. they possess comparatively low corrosion resistance. This loss in corrosion resistance is probably caused by the removal of a large amount of chromium from the matrix, owing to the precipitation of the chromium carbide, Cr_4C . The finely dispersed state taken by the precipitate may be assumed to contribute to this effect.

It may thus be seen that a study of the various carbides and the temperatures and compositions at which they exist appears to offer a system of classification from which conclusions may be drawn concerning the properties of the steels that form the carbides in question. At least with respect to some properties, such a system would appear to be already definitely established.

The influence of vanadium and of the other carbide-forming elements may, in conclusion, be summarized as follows:

As a consequence of the abstraction of carbon from the matrix by the formation of the special carbide, the hardening power of the steel when quenched from the usual temperatures generally is low, because the special carbide is less soluble in austenite than iron carbide. At higher quenching temperatures, owing to the retarding action exerted by the carbide particles on grain growth, vanadium steels are not susceptible to overheating. The increasing solution of the carbide on increasing temperature diminishes the critical rate of cooling, and accordingly increases the depth of penetration of the hardness. On tempering, the special carbide of low solubility separates from the alpha iron only at high tempering temperatures and, by a sort of precipitation-hardening, increases the stability of hardness of the steel to the tempering treatment. The phenomena involved can be represented in the manner shown in Fig. 22. The martensite formed by the gamma-alpha transformation causes a decrease in hardness during the tempering just as in simple iron-carbon alloys, as shown by curve 1. The precipitation of the special

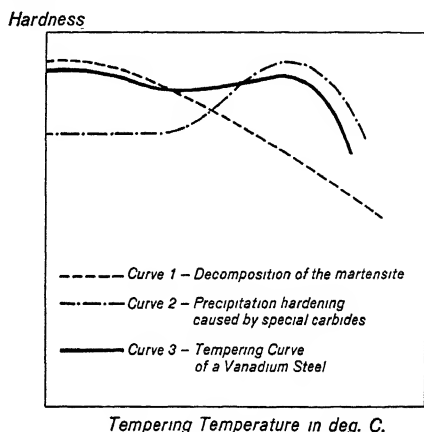


FIG. 22.—DIAGRAM REPRESENTING SUPERPOSED PHENOMENA THAT OCCUR ON TEMPERING VANADIUM STEEL QUENCHED FROM HIGH TEMPERATURE.

carbide at higher temperatures brings about an increase in hardness as shown by curve 2. The combination of the two phenomena gives curve 3, synthesized from curves 1 and 2. This curve 3 corresponds exactly to the one with which we are familiar in connection with high-alloy steel, particularly high-speed tool steel. For such steels, however, the secondary increase in hardness can also be ascribed to the transformation of the residual austenite into martensite. This transformation, however, is practically completed after one heating to 550° to 600° C. and subsequent cooling; furthermore, the newly formed martensite would become soft very quickly at high cutting temperatures if it were not hardened by the precipitation of the special carbides. It is safe, therefore, to conclude that the secondary increase in hardness occurring in high-speed steels is due not only to precipitation-hardening but also probably in part to the transformation of residual austenite, whereas the stability of the martensitic hardness up to 600° C., the red-hardness, is exclusively due to the fact that special carbides precipitate and coagulate at higher temperatures than cementite.

Linear Thermal Expansion and Transformation Phenomena of Some Low-carbon Iron-chromium Alloys

BY J. B. AUSTIN* AND R. H. H. PIERCE, JR.*

(New York Meeting, February, 1935)

IN developing a consistent picture of the thermal expansion of the commercial chromium steels, which cover a range of carbon contents, it is desirable to know the expansion in the limiting case of the binary, carbon-free, iron-chromium alloys. We have, therefore, determined the thermal expansion of a series of five special alloys, ranging in chromium content from 3 to 10.5 per cent, with not more than 0.03 per cent carbon, over a temperature range extending beyond the transformation region; this low carbon content enables us to draw reasonably reliable conclusions as to the behavior of the carbon-free system. Moreover, the measurements serve to determine the beginning and the end of the alpha-gamma transformation; and they emphasize once more the fact that a transformation temperature determined by any method in which the specimen is cooled at an appreciable rate is apt to be seriously in error, particularly if the metal contains a transformation-retarding element such as chromium or manganese. The lag, or undercooling, observed at the $\gamma - \alpha$ transformation is explained in terms of the influence of temperature on transformation velocity; the rather unusual shape of the γ loop is attributed to a change with temperature and with composition of the distribution of chromium between the alpha-iron and gamma-iron solid solutions.

The exact composition of the alloys, which were obtained through the courtesy of Dr. W. Rohn, of the Heraeus Vakuumschmelze A-G., is given in Table 1. Determinations of the linear thermal expansion and of transformation temperature were carried out in the vacuum dilatometer previously described,¹ using a rate of heating and of cooling of 3.0° to 3.5° per minute unless otherwise stated. Magnetic susceptibility, which was measured in studying the rate of transformation, was determined with a magnetic balance, which also has been described.²

RESULTS AND DISCUSSION

Thermal Expansion Coefficients.—Numerical values for the linear expansion coefficient, derived from a smoothed curve based on at least

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¹ Austin: *Physics* (1932) **3**, 240.

² Sosman and Austin: *Jnl. Wash. Acad. Sci.* (January, 1935).

30 experimental points for each alloy, are given in Tables 2 and 3, which contain respectively the mean coefficient, α_m , between 20° and t° , and the

TABLE 1.—*Composition of the Alloys*

| Alloy No. | Percentages | | | |
|-----------|-------------|-------|------|-------|
| | Cr | C | Si | N |
| 1 | 3.25 | 0.026 | 0.16 | 0.032 |
| 2 | 4.96 | 0.030 | 0.23 | 0.057 |
| 3 | 7.18 | 0.020 | 0.10 | 0.049 |
| 4 | 9.02 | 0.028 | 0.11 | 0.046 |
| 5 | 10.58 | 0.022 | 0.07 | 0.050 |

TABLE 2.—*Mean Linear Expansion Coefficient $\alpha_m \times 10^6 (l_t = l_0(1 + \alpha_m t))$*

| $t^\circ \text{ C.}$ | No. 1 | No. 2 | No. 3 | No. 4 | No. 5 |
|----------------------|--------------------|-------|-------|-------|-------|
| | Chromium, Per Cent | | | | |
| | 3.25 | 4.96 | 7.18 | 9.02 | 10.58 |
| 50 | 11.4 | 11.4 | 11.7 | 11.0 | 11.2 |
| 100 | 11.6 | 11.4 | 11.8 | 11.1 | 11.3 |
| 150 | 11.9 | 11.5 | 11.9 | 11.2 | 11.4 |
| 200 | 12.1 | 11.5 | 12.0 | 11.3 | 11.5 |
| 250 | 12.4 | 11.6 | 12.1 | 11.4 | 11.6 |
| 300 | 12.6 | 11.7 | 12.2 | 11.5 | 11.7 |
| 350 | 12.8 | 11.9 | 12.3 | 11.6 | 11.8 |
| 400 | 13.0 | 12.1 | 12.5 | 11.8 | 11.9 |
| 450 | 13.2 | 12.4 | 12.7 | 12.0 | 12.1 |
| 500 | 13.4 | 12.6 | 12.8 | 12.2 | 12.3 |
| 550 | 13.5 | 12.8 | 12.9 | 12.3 | 12.4 |
| 600 | 13.6 | 12.9 | 13.0 | 12.4 | 12.4 |
| 650 | 13.7 | 13.0 | 13.0 | 12.4 | 12.4 |
| 700 | 13.7 | 13.1 | 13.1 | 12.4 | 12.4 |
| 750 | 13.8 | 13.2 | 13.1 | 12.5 | 12.5 |
| 800 | 13.8 | 13.2 | 13.2 | 12.5 | 12.6 |

true, or instantaneous, coefficient α_t at t° . The influence of temperature on the true coefficient of three of the alloys is also shown in Fig. 1, from which it is evident that the maximum coefficient at approximately 450° C. appearing so markedly in the expansion of pure iron³ is carried over into these chromium alloys. The minimum coefficient observed

³ Austin and Pierce: *Trans. Amer. Soc. Metals* (1934) **22**, 447.

at the magnetic inversion (A_2 or Curie point) in pure iron does not, however, appear in these alloys, which presumably are too stiff to yield to

TABLE 3.—*True Linear Expansion Coefficient $\alpha_t \times 10^6$*

$$\alpha_t = \frac{1}{l_0} \frac{dl}{dt}$$

| $t^\circ \text{C.}$ | No. 1 | No. 2 | No. 3 | No. 4 | No. 5 |
|---------------------|--------------------|-------|-------|-------|-------|
| | Chromium, Per Cent | | | | |
| | 3.25 | 4.96 | 7.18 | 9.02 | 10.58 |
| 50 | 11.5 | 11.2 | 11.0 | 10.9 | 11.0 |
| 100 | 12.0 | 11.4 | 11.4 | 11.1 | 11.3 |
| 150 | 12.5 | 11.6 | 11.8 | 11.3 | 11.6 |
| 200 | 13.0 | 11.8 | 12.2 | 11.5 | 12.0 |
| 250 | 13.5 | 12.2 | 12.6 | 11.9 | 12.4 |
| 300 | 14.0 | 12.8 | 13.0 | 12.5 | 12.8 |
| 350 | 14.5 | 13.7 | 13.6 | 13.4 | 13.2 |
| 400 | 15.2 | 14.2 | 14.0 | 13.9 | 13.6 |
| 450 | 15.1 | 14.5 | 14.1 | 13.8 | 13.6 |
| 500 | 14.8 | 14.6 | 14.1 | 13.7 | 13.4 |
| 550 | 14.6 | 14.5 | 14.0 | 13.5 | 13.1 |
| 600 | 14.5 | 14.3 | 13.9 | 13.3 | 12.8 |
| 650 | 14.5 | 14.2 | 13.8 | 13.1 | 13.0 |
| 700 | 14.5 | 14.0 | 13.7 | 13.0 | 13.4 |
| 750 | 14.5 | 13.9 | 13.6 | 12.9 | 13.8 |
| 800 | 14.4 | 13.9 | 13.6 | 12.8 | 14.2 |
| In gamma form.... | 19.8 | 20.0 | 20.0 | 19.0 | 19.9 |

this effect. The curious minimum in the curve for the 10.5 percent chromium alloy (Fig. 1) does not coincide with the A_2 temperature and

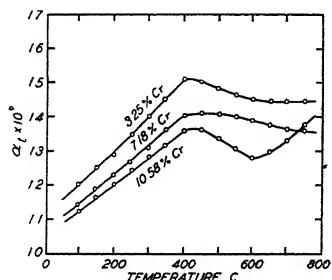


FIG. 1.

FIG. 1.—INFLUENCE OF TEMPERATURE ON TRUE LINEAR EXPANSION COEFFICIENT OF IRON-CHROMIUM ALLOYS.

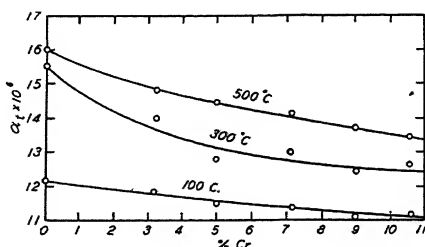


FIG. 2.

FIG. 2.—INFLUENCE OF CHROMIUM CONTENT ON TRUE LINEAR EXPANSION COEFFICIENT OF IRON-CHROMIUM ALLOYS.

cannot be explained in this way; in fact, we have found no satisfactory explanation for it.

No extensive data on the expansion coefficient of alloys covering the same range of chromium content and of comparable purity are available in the literature, but there are a few measurements by Ruf⁴ and by Stäblein,⁵ which can be used for comparison. Ruf's values fall somewhat lower than those given in Table 2, while Stäblein's are in fair agreement with them. Data on alloys containing higher carbon have been reported by Matsushita⁶ and by Hidnert,⁷ and a comparison of our values with

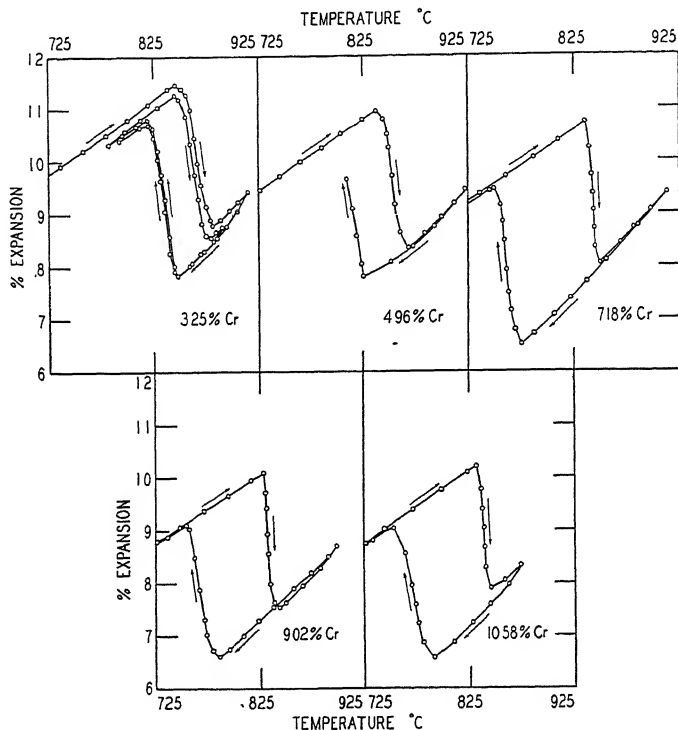


FIG. 3.—DILATATION OF ALLOYS IN PASSING THROUGH ALPHA-GAMMA TRANSFORMATION.

theirs gives some indication that the expansion coefficient increases with carbon content, but the evidence is not conclusive.

The influence of chromium on the true expansion coefficient at several temperatures is shown in Fig. 2, which includes, for comparison, data on a sample of iron of about the same purity as that used in the alloys. The decrease in coefficient with increasing chromium content is in qualitative agreement with the data of previous investigators; quantitatively it is in fair agreement with the extrapolated curves of Hidnert, but falls below

⁴ Ruf: *Ztsch. Elektrochem.* (1928) **34**, 813.

⁵ Stäblein: *Archiv f. d. Eisenhüttenwesen* (1929-30) **3**, 301.

⁶ Matsushita: *Sci. Repts. Tōhoku Imp. Univ.* (1920) **9**, 243.

⁷ Hidnert: *U. S. Bur. Stds. Jnl. of Research* (1932) **7**, 1031.

Matsushita's and above Ruf's. Since our alloys were very low in carbon, we have not been able to check the irregularities found by Matsushita below 3 per cent chromium and ascribed by him to the presence of carbides.

The influence of chromium on the true expansion coefficient of these alloys in the gamma form, which is shown in Table 3, appears to be much less than when they have the alpha structure. In fact, the gamma coefficient is practically constant, although appreciably lower than that of pure iron, indicating that the lowering of the coefficient is brought about by the first small additions of chromium and that further additions are not as effective.

Change in Length at A_3 .—The behavior of the several samples in passing through the alpha-gamma transformation in each direction, at a

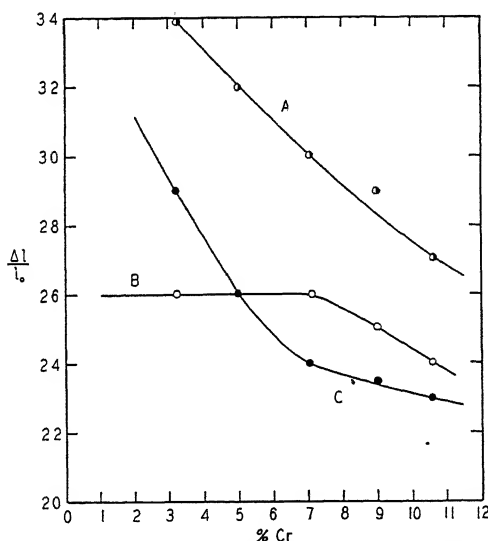


FIG. 4.—INFLUENCE OF CHROMIUM CONTENT ON CHANGE IN LENGTH AT ALPHA-GAMMA INVERSION AS GIVEN IN FIG. 3.

rate of temperature change of close to 3.5° C. per minute, is shown in Fig. 3. In order to render the influence of chromium on the change in length occurring during this transformation more apparent, values of $\Delta l/l_0$ as shown in Fig. 3 have been read off and plotted against chromium content in Fig. 4. Curve A represents the change calculated at the beginning of each transformation; that is, it is the distance, at this temperature, between the curve for an alloy in the alpha form and the extrapolated curve for the gamma form. Curve B gives the net change in length as observed; that is, the actual change that is found in the length of the sample as it is heated through the transformation (or the distance between the maximum and minimum points on the curve). Curve C gives the change for 925° C. calculated by extrapolating the

alpha curve to that temperature, and is the line that can be compared with $\Delta l/l_0$ for pure iron. If this curve is extrapolated to zero chromium, the value obtained is considerably higher than results previously reported,⁸ but there is always the possibility that the curve will flatten out as chromium is diminished (as in curve *B*), so that too great weight can not be given to the extrapolation.

Alpha-gamma Transformation Temperatures.—In attempting to construct the gamma loop of the equilibrium diagram from the data in Fig. 3, or for the values in Table 4 that are based on the curves of Fig. 3, one is immediately faced with the difficulty of choosing between the widely different A_3 temperatures observed on heating and on cooling. This discrepancy, which has been universally observed, has for a long time left an element of uncertainty in the exact position of the gamma loop. For instance, Adcock,⁹ in his careful study of this system obtained

TABLE 4.—*Alpha-gamma Transformation Temperatures as Shown by Dilatometer Curves (Fig. 3)*

| Sample No. | Cr, Per Cent | Acs, Deg. C. | | Ars, Deg. C. | |
|------------|--------------|--------------|-----|--------------|-----|
| | | Start | End | Start | End |
| 1 | 3.25 | 845 | 880 | 845 | 820 |
| 2 | 4.96 | 840 | 868 | 825 | |
| 3 | 7.18 | 835 | 850 | 775 | 750 |
| 4 | 9.02 | 828 | 838 | 785 | 755 |
| 5 | 10.58 | 833 | 845 | 792 | 752 |

a persistent hysteresis of this type, which he was unable to eliminate by a moderate variation in the rate of change of temperature, so that he took an average value in the construction of his constitutional diagram, a procedure which, while undoubtedly expedient, is admittedly somewhat unsatisfactory. A reasonable explanation of these differences appears, however, to be provided by the data obtained in the past few years on the velocity of decomposition of austenite. Thus, it has been shown by Davenport and Bain¹⁰ that this velocity can be represented as a function of temperature by a curve such as is shown in Fig. 5, which is taken from their paper; and their examination of a number of steels demonstrated that this shape is generally obtained, although the curve as a whole may be shifted along the time axis with a change in composition. The interesting part of this curve from the point of view of this discussion is the "nose" in the upper part, which indicates that just below the equilibrium

⁸ Austin and Pierce: Reference of footnote 3.

Esser and Müller: *Archiv f. d. Eisenhüttenwesen* (1933-34) **7**, 265.

⁹ Adcock: *Jnl. Iron and Steel Inst.* (1931) **124**, 99.

¹⁰ Davenport and Bain: *Trans. A.I.M.F.* (1930) **90**, 117.

temperature the velocity is small and the period of induction—the time interval¹¹ required for the reaction to produce a measurable amount of

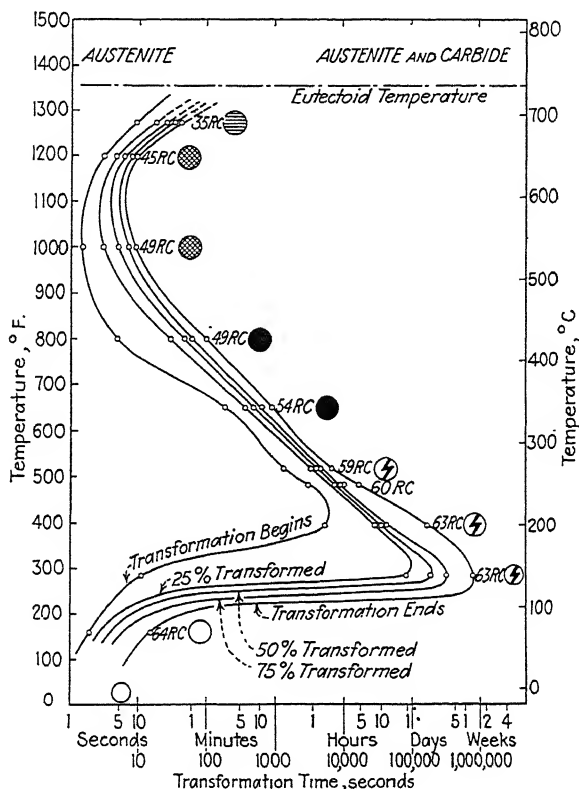


FIG. 5.—TYPICAL CURVE SHOWING RATE OF TRANSFORMATION OF AUSTENITE TO FERRITE. (FROM DAVENPORT AND BAIN.)
Actual data for a steel containing 1.17 carbon.

ferrite—is very long, and that with decreasing temperature this interval decreases, passes through a minimum, then increases again.

A similar time-temperature chart can be constructed to show the beginning and end of transformation at various cooling rates instead of at

¹¹ This time interval obviously is dependent on the precision of the method by which the progress of the reaction is observed, and it is believed that in most of the cases discussed here some change does occur before the apparent start of the reaction as measured by the means described; therefore the term "period of induction" is to a large extent an arbitrary one. Nevertheless, it has a definite meaning if the experimental conditions are specified and has an unquestionable usefulness in developing the general concept so that its use is considered justified. It is, of course, possible that there are cases in which the reaction does not really begin for a definite period, but these are probably special instances rather than the general rule.

various constant temperatures.¹² Such a curve should give the transformation temperature for any rate at which the metal is cooled, and for reasonably slow rates of cooling this curve ought to lie somewhere near the constant-temperature curve, although it will be displaced in the direction of a longer time interval because the metal has spent part of its cooling time in a temperature zone in which the period required for the formation of a recognizable amount of ferrite is longer. It must be strongly emphasized that the constant-temperature chart and the curve correlating behavior at different cooling rates, while similar in some respects are widely different in others, and the differences are serious or not depending on the viewpoint. In considering hardenability the differences are tremendous and great care should be exercised to distinguish between the two curves; yet when dealing with the lag to be expected in the transformation temperature at rates of cooling less than, say, 30° or 40° a minute, the constant-temperature curve will have the same general shape as the one for various cooling rates and may be useful as a first approximation to it.

In order to test these conclusions and to show the relation between the lag in the apparent start of the A_3 transformation on cooling and the reaction velocity chart, a part of the constant-temperature curve for the 9 per cent chromium alloy has been determined by means of a magnetic balance and the results have been compared with the A_3 temperatures observed with the dilatometer. A small piece of the alloy, sealed in a vitreous silica tube evacuated to 0.01 mm. mercury or less, after being soaked for some minutes in a small electric furnace heated to just above the equilibrium A_3 temperature, was quickly transferred to the hot furnace of the magnetic balance referred to in the section on apparatus. The change of the magnetic susceptibility of the alloy with time was then determined. Since the paramagnetism of austenite is relatively feeble (mass susceptibility about 24×10^{-6}) the appearance of a very small quantity of the strongly paramagnetic ferrite (susceptibility well above 300×10^{-6} at the temperatures employed) was easily detectable and the progress of the transformation could be conveniently followed. It was not always possible to follow the reaction to completion because ferrite formed at temperatures below its Curie point (A_2) has such a large susceptibility that a completely transformed specimen was "too magnetic" for our apparatus. This limitation is not serious, however, since the initial stages of transformation are more important for our purpose than the end. The results of these measurements, shown in Fig. 6,

¹² See, for example, those given by Bain in *Trans. Amer. Soc. Steel Treat.* (1932) **20**, 390, and in Fig. 3 in his paper on Some Characteristics Common to Carbon and Alloy Steels, presented before the American Iron and Steel Institute at New York, May 24, 1934.

suffice to fix the upper part of the constant-temperature transformation curve for this alloy.

The diagram also shows the time-temperature curve for a cooling rate of 3° per minute, a rate very close to the average rate of cooling used in the dilatometer. This curve represents the time-temperature path followed by the samples in cooling and has marked upon it the points at which the gamma-alpha transformation appeared to begin, and was completed, in this alloy as measured by the change in length of the sample examined. The first of these points fixes the intersection of the time-temperature path with the curve for the appearance of a recognizable

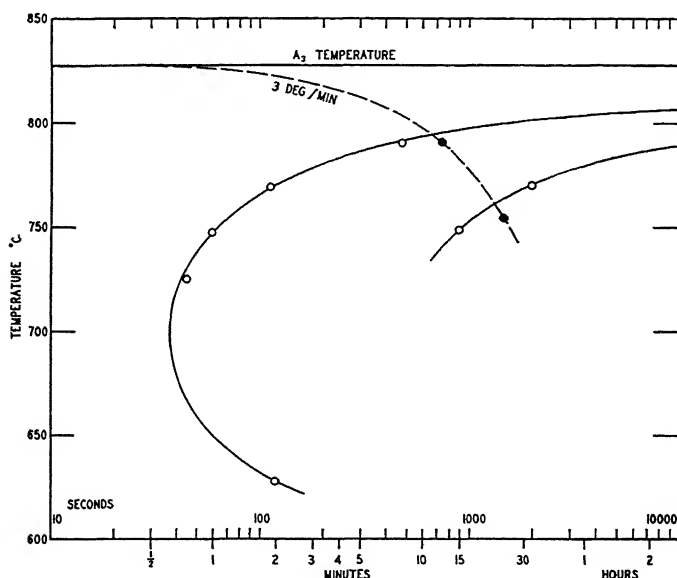


FIG. 6.—RATE OF TRANSFORMATION OF AUSTENITE TO FERRITE IN ALLOY No. 4 (9 PER CENT CR).

quantity of ferrite at different rates of cooling, and it is to be observed that, even making allowance for the logarithmic time scale, the points are in fair agreement with the constant-temperature curve, lying, as they should, somewhat to the right of the curve. This concordance indicates that the undercooling observed in the A_3 temperatures is associated with the low velocity of transformation of austenite just below the equilibrium and further shows that, if a chart for different rates of cooling is not available, an approximation to the lag can be obtained from the constant-temperature curve.

One example of the usefulness of an estimate of this sort is in indicating the serious errors that may be made in the determination of equilibrium diagrams by any method involving cooling. For example,

relatively few thermal analyses are made with a rate of cooling as low as 3° per minute, and yet in the 9 per cent chromium alloy the error for this rate is almost 40° C. Plotting time-temperature paths for other rates with this same alloy shows that even with a rate as low as 0.5° per minute the error will be of the order of magnitude of 20° C. Even when the method of quenching specimens held for a long time just below the equilibrium temperature is employed it must be used with care because this alloy containing 9 per cent chromium showed no magnetically measurable amount of ferrite even after 8 hr. at a temperature only 12° C. below its A_{c3} temperature. In this connection it is interesting to note that Bain, Davenport and Waring in their study of the Fe-C-Mn alloys found that in some cases alloys held just a few degrees below the equilibrium temperature required 1000 hr. for complete transformation. These last facts emphasize a point that has long been established in the field of inorganic chemistry, and which has been recognized by experienced investigators of metal systems; namely, that the only safe way to determine an equilibrium datum is to approach the equilibrium from both sides.

The errors just discussed will be diminished, of course, with decreasing chromium content, as is indicated by the decreasing discrepancy between the A_{c3} and A_{r3} temperatures in Table 4, but the curve of Fig. 5 shows that an appreciable error can be made even in plain carbon steels. In this connection, it is to be noted that these data point to the conclusion that as pure iron is approached the lag in the A_{r3} temperature becomes less, a view that supports one of the criteria of purity used in our study of pure iron;¹³ namely, that the purest sample has the smallest difference between the A_{c3} and A_{r3} temperatures.

In the light of the evidence just presented it has been considered justifiable to discard the A_{r3} temperatures entirely in constructing the gamma loop in the equilibrium diagram. This leaves the A_{c3} data and the question arises as to how much lag there is on heating. It is now generally admitted that the lag on heating is much smaller than that on cooling, but in order to get a direct comparison between the order of magnitude of superheating and of undercooling, a few observations were made on the rate of transformation of ferrite, at a constant supercritical temperature, in the alloy containing 11 per cent chromium, which one would expect to have the slowest reaction rate of the whole series. The technique was the same as that used in determining the data shown in Fig. 6, except that the metal was soaked just below the equilibrium temperature and was then quickly transferred to the magnetic balance whose furnace was heated to a temperature just above the equilibrium value. These measurements showed that when this alloy was held

¹³ Austin and Pierce: Reference of footnote 3.

8° above the Ac_3 point determined by the dilatometer, ferrite appeared within 20 sec., about the lower limit of measurement for the method used, and that the sample was almost completely ferritic within 90 sec. These intervals were relatively so short that high precision in measuring them was not possible, but they are sufficiently accurate to show that the lag on heating is very much smaller than that on cooling and should not exceed 3° to 4° C. at the most. For alloys containing less chromium this lag is certain to be less (although Sato's¹⁴ data on carbon steels indicate that the influence of composition is not so marked in overheating as in undercooling) and the Ac_3 temperature probably gives a close approximation to the equilibrium value. The temperatures at which the dilatation curves show a break on heating have therefore been used to fix the lower curve of the gamma loop (solid line in Fig. 7) with the realization that they may be several degrees high.

Two-phase Region of the Gamma Loop.—It has long been recognized from phase-rule considerations that the gamma loop should be bounded by a two-phase region, and clear indications of its existence have been found from time to time; as, for example, in the high-temperature X-ray studies of Oberhoffer and Esser.^{14a} But so far as we are aware the only diagram showing the two-phase region that is based on direct experimental evidence is that of Bain and Aborn in the National Metals Handbook for

1933 (p. 1451). They observed the change in length in the neighborhood of the transformation of the same alloys used in this investigation by means of an apparatus similar to that described by Bain and Waring.¹⁵ In this case, however, the dilatometer was fitted with a fused silica feeler and pedestal and was enclosed in a furnace of which the temperature was read by a thermocouple of fine wire attached to the specimen. In making the observations the temperature was allowed to come to equilibrium; the length, which could be read, to 0.0002 in., was noted, and the temperature was then raised by approximately 5° C. In this way it was possible to follow the change in length of the specimens as they passed through the inversion. Actual coefficients of expansion

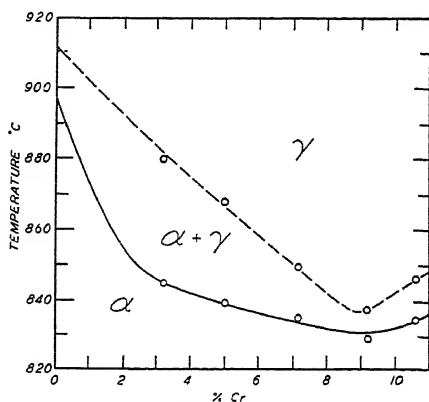


FIG. 7.—GAMMA LOOP AND TWO-PHASE REGION FOR IRON-CHROMIUM ALLOYS CONTAINING APPROXIMATELY 0.02 PER CENT CARBON. BASED ON CURVES SHOWN IN FIG. 3.

¹⁴ Sato: *Tech. Repts.* Tohoku Imp. Univ. (1928) 8, 27.

^{14a} Oberhoffer and Esser: *Stahl u. Eisen* (1927) 47, 2021.

¹⁵ Bain and Waring: *Trans. Amer. Soc. Steel Treat.* (1929) 15, 69.

were not sought and creep in the silica was neglected. A slight thermal gradient existed in the specimen (about 5°C.), therefore, because the temperature recorded was the highest, the A_1 point was more accurately measured than the A_3 . The gradual contraction on heating took place over a range of some 20° or 25°C. , indicating a two-phase region of which the temperature limits are not greatly different from those reported here. They also rejected the Ar points as characteristic only of the undercooling in these alloys even when the effective cooling rate was close to zero.

Additional data from which the limits of this region can be derived are available in the curves of Fig. 3. Considering only the heating curves, which has already been shown to be the only justifiable procedure, it is seen that in every case the transformation starts sharply, leaving no doubt as to the temperature of the lower limit of the loop for the several samples. There is also in every case an appreciable temperature interval or, since the rate of heating was approximately constant, a time interval during which the transformation takes place, but the striking and significant thing is that this interval varies in a regular manner. With increasing chromium content it increases (the dilatation curves become steeper), then decreases, passes through a minimum and again increases. This is important for two reasons: (1) because the intervals correspond fairly well with those obtained by Bain and Aborn, which indicates that these intervals are closely associated with the limits of the two-phase region; and (2) because a decrease in these intervals with change of concentration at a constant rate of heating denotes approach to a pure substance, or to a eutectic, or to a maximum or minimum in the curve considered. In this case a minimum is clearly indicated by the lower limit of the loop, and since, as will be shown in the next section, the two-phase region vanishes at the minimum in the loop for pure Fe-Cr alloys, it is certainly no coincidence that the minimum interval should correspond with the minimum temperature of the loop. In other words, it is believed that the upper limit of the transformation interval in the curves of Fig. 3 is very close to the upper limit of the two-phase region for each alloy.

An independent confirmation of this conclusion has been obtained from the variation of the magnetic susceptibility (X) of these alloys in passing through the inversion, which was determined by means of the magnetic balance used in measuring the rate of decomposition of austenite. The alloys, protected against oxidation as before by being sealed in a small silica tube under a pressure of approximately 10 microns, were held at each temperature for a length of time that experience indicated as sufficient to allow equilibrium to be attained, usually 10 to 15 min. The results, given in Fig. 8, and a comparison of the behavior of the 3.25 per cent chromium alloy with that of a sample of iron corre-

sponding to the one used in making the alloys (Fig. 9), show clearly that the curves for these alloys depart distinctly from that to be expected of

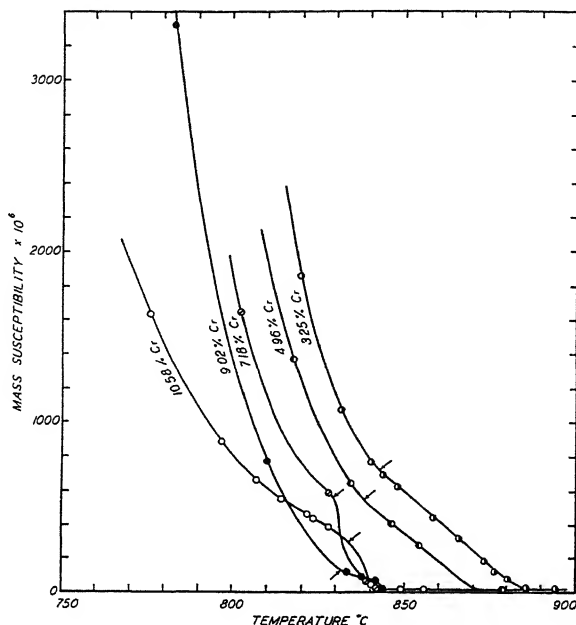


FIG. 8.—EFFECT OF TEMPERATURE ON MAGNETIC SUSCEPTIBILITY OF IRON-CHROMIUM ALLOYS.

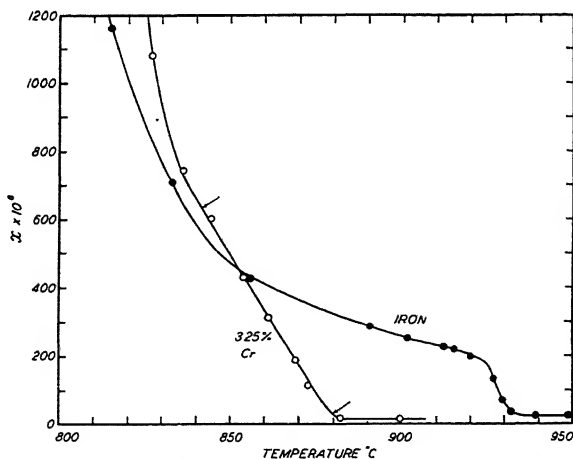


FIG. 9.—COMPARISON OF TEMPERATURE VARIATION OF MAGNETIC SUSCEPTIBILITY OF A METAL PASSING DIRECTLY FROM ALPHA TO GAMMA (IRON) AND ONE THAT HAS AN APPRECIABLE TWO-PHASE REGION.

a metal having a sharp transformation. Thus, after following the Curie-Weiss law (X , is inversely proportional to the temperature measured

above the magnetic inversion) for a considerable temperature interval, the susceptibility begins to decrease more rapidly than the law predicts at a temperature considerably below that at which the inversion is complete, indicating the disappearance of ferrite over an appreciable range of temperature. In Fig. 8 the temperature at which this departure becomes recognizable is indicated on each curve by an arrow; the temperature at which the transformation is complete is clear without any special designation. In the case of the alloys containing 3.25 per cent and 5.00 per cent chromium, the temperature limits of this region in which ferrite disappears are clearly defined, and are in surprisingly good agreement with those determined with the dilatometer. For the other alloys the transformation takes place over a shorter interval and the limits are not so definite; but although not so precise, they are entirely consistent with the conclusions drawn from the expansion data. Moreover, they are entirely reasonable and in accord with the schematic diagram deduced from the phase rule. It is believed, therefore, that these data yield the boundaries of the two-phase region, and the gamma loop showing this region for the alloys examined is given in Fig. 7. Table 1 shows that these alloys contain an appreciable quantity of impurities, of which the most serious in its effects is, perhaps, the carbon, so that the diagram we are considering should be taken as a constant carbon slice through the ternary system Fe-Cr-C, or it may belong to an even more complex system. The two-phase region will not, therefore, show quite the form that it would for pure Fe-Cr alloys, since the two-phase region will not vanish at the pure iron axis nor at the minimum, but will be as in Fig. 7, in which the data for zero chromium have been taken from a sample of iron of purity comparable to that used in making the alloys.

Since in our study of pure iron the purest samples showed a transformation interval of 4° or 5° , the upper curve may be high by that much. Therefore it has been made a dashed line to indicate this uncertainty, although it is believed that its position is substantially correct as shown, except possibly close to the iron axis.

Shape of Gamma Loop.—The existence of a minimum in the lower part of the gamma loop makes this system very interesting from a thermodynamic point of view; for although this type of curve is unique among the solid binary alloys thus far investigated it is by no means uncommon in inorganic salt systems, or even in liquid metal systems. Indeed, the liquidus and solidus curves in this very system show a minimum of this type, which thermodynamically is in every way equivalent to the lower part of the gamma loop in the solid.

We have already pointed out, in connection with pure iron, that the change with composition of the transformation temperature (which may be a solid-solid transition or a solid-liquid transition) in a dilute solution (liquid or solid) can be represented by the equation:

$$\frac{dT}{dN_2} = \frac{RT^2}{\Delta H}(K - 1) \quad [1]$$

where dT is the change in transformation temperature T (on the absolute scale) with N_2 , the mol fraction of solute in the gamma phase, R is the gas constant per mol of solvent, ΔH is the molar heat of transition and K is the distribution coefficient of the solute between the two phases; that is, the ratio of the equilibrium concentration of solute in the low-temperature phase to that in the high-temperature phase at the same temperature; all these quantities being expressed in the appropriate units. The alloys considered here are hardly dilute solutions, nor are they truly binary, hence equation 1 would not be expected to hold quantitatively, yet it offers good means of explaining the shape of the gamma loop qualitatively.

It should be noted at the start that the sign of dT is determined by the factor $K - 1$; for R and T are obviously positive at all times and there is ample evidence to show that ΔH is positive in all the cases considered. Therefore, if K is greater than 1; that is, if the concentration of solute in the low-temperature phase is greater than that in the high-temperature phase, dT is positive, or the transformation temperature is raised. On the other hand, if K is less than 1, dT is negative and the transition temperature is lowered. For the case of identical solubility in each phase $K = 1$ and $dT = 0$; that is, the tangent to the curve of transition temperature against composition will be horizontal.

In most of the binary ferrous alloys, the solute is either more soluble in the gamma phase at all temperatures and all compositions of the solutions or more soluble in the alpha phase at all temperatures and all compositions of solutions, which means that if K is less than one at A_3 it is greater than one at A_4 , and if it is greater than one at A_3 it is less than one at A_4 . Consequently if the A_3 point is lowered the A_4 point is raised and the constitutional diagram of the system shows the enlarged austenite field characteristic of a so-called "austenite stabilizing" alloying element; or conversely, if the A_3 point is raised, the A_4 point is lowered and the constitutional diagram shows a closed gamma loop and the alloying element is said to stabilize ferrite.

There is no *a priori* reason, however, why the distribution coefficient K should not change with temperature or with composition, and, indeed, it appears to do so in the iron-chromium system, because at low chromium contents both A_3 and A_4 transformations are lowered by the addition of more chromium, which means that at 900° C. chromium is more soluble in the gamma phase ($K < 1$) while at 1400° C. it is more soluble in the alpha phase (again $K < 1$). As the chromium content of the two phases increases, the distribution coefficient at the lower temperature increases, approaching unity, whereas at the higher temperature it seems to diminish a little. This change continues until at the lower

temperature K becomes equal to one; that is, chromium is equally soluble in the two phases, the tangent to the temperature-composition curves becomes horizontal and the curve itself is at a minimum. With still further additions of chromium, K becomes greater than one over the whole temperature range and the A_3 curve swings up to meet the A_4 curve. Equation 1 gives us therefore a consistent picture of the behavior in the iron-chromium system

The validity of this picture can be checked by a consideration of the geometry of the gamma loop and its two-phase boundary. Thus, if it is found experimentally that the A_3 curve falls with increasing chromium content, the only possible way in which the two-phase region can be drawn is with a higher percentage of chromium in the gamma phase ($K < 1$); if, on the other hand, the A_3 temperature is raised, the two-phase region can only be drawn with the alpha phase richer in chromium

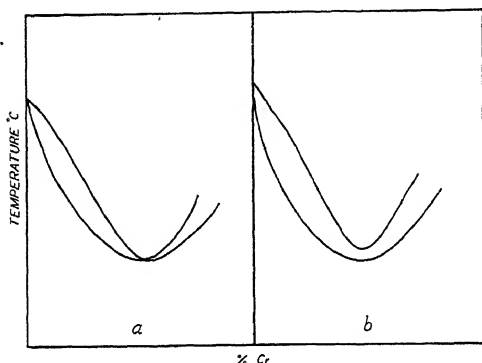


FIG. 10.—SCHEMATIC DIAGRAMS FOR SHAPE OF GAMMA LOOP (a) IN A BINARY SYSTEM, AND (b) IN A TERNARY SYSTEM.

($K > 1$). When the minimum point in the curve is considered ($K = 1$) the matter is not quite so simple because there are two possibilities, as shown in Fig. 10. For a true binary system the upper and lower curves start from a single point on the pure iron axis, diverge, then meet again at the minimum as shown in *a*, and as drawn in the diagram of Bain and Aborn; but in a ternary or higher system the two curves do not meet at the plane of zero chromium nor will they necessarily be tangent to each other at the minimum but will have a position such as is shown schematically in *b*. Since our alloys are not a true binary system we have drawn our loop in Fig. 7 in the form of Fig. 10*b*.

It should be noted in this connection that if a sufficient quantity of a third component is added the value of K may be so altered, even at low chromium contents, that the minimum in the gamma loop does not appear. Carbon seems to be particularly effective in this respect; the presence of several tenths of one per cent is sufficient to make chromium more soluble in ferrite than in austenite at approximately 900° C. and the minimum

does not appear in the loop of a constant carbon slice of the Fe-Cr-C system. This fact explains the observations of early investigators of this system, which showed no minimum because of the carbon present in the alloys.

It is also interesting to note that the minimum in the gamma loop of the binary Fe-Cr system permits the existence at one temperature of two sets of alpha and gamma phases of different composition. Thus, if chromium is added to iron at 850° C., assuming always that sufficient time is allowed for equilibrium to be attained, there will be at first a single solid solution (ferrite). At about 3 per cent chromium, a second phase (austenite) containing 7 per cent chromium will appear; as more chromium is added, the proportions but not the compositions of these

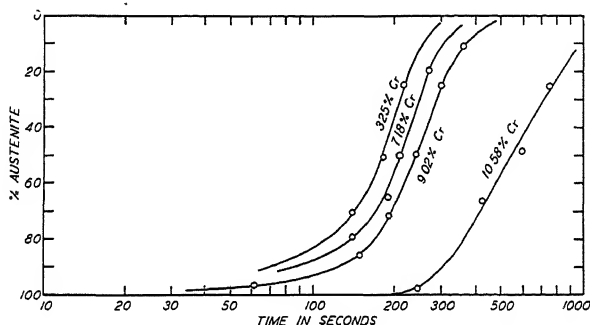


FIG. 11.—RATE OF TRANSFORMATION OF AUSTENITE TO FERRITE IN FOUR ALLOYS.

phases will change, the austenite growing at the expense of the ferrite. When 7 per cent chromium has been added the metal again will be a single homogeneous phase, which will persist until approximately 11 per cent chromium is present, when ferrite containing a higher content of chromium appears. Again the proportions, but not the compositions, of the two phases change until finally the alloy is again a homogeneous solid solution-ferrite. This behavior, which has long been recognized in organic and inorganic systems, and even in liquid metals, means that at certain temperatures there are two distribution coefficients and that the distribution coefficient is therefore influenced by the total composition of the system.

Rate of Gamma-alpha Transformation on Cooling.—The dilatometer curves representing the gamma-alpha transformation on cooling can also be used to estimate the rate of transformation of the alloys at subcritical temperatures. If the rate of cooling is taken as 3° per minute the temperature ordinates can be converted into a time scale, and if it is assumed that the percentage of austenite transformed at any given time is proportional to the fraction of the total change in length that has occurred at that time, the progress of the reaction can be followed easily. This has been done in Fig. 11 with results very much like the curves for nickel

and manganese alloys given by Bain.¹⁶ Obviously they are not as accurate as his because the temperature was not held constant; nevertheless they show that these alloys do fit into the general picture of reaction rates as given by Bain.

Tammann¹⁷ has further shown that if Bain's curves for the nickel and manganese alloys are plotted in terms of the ratio of the elapsed time to the time required for the transformation of 50 per cent of the austenite,

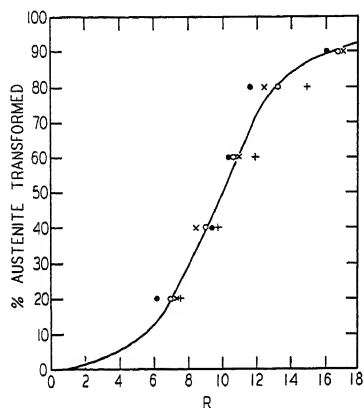


FIG. 12.—CURVES OF FIG. 11 SHIFTED SO AS TO COINCIDE AT TRANSFORMATION OF 50 PER CENT AUSTENITE.

rather than elapsed time itself, the data can be represented by a single curve. This is true also of the chromium alloys, as is evident from Fig. 12, in which the curves of Fig. 11 are replotted on the fractional time scale.

SUMMARY

1. The linear thermal expansion of five iron-chromium alloys of low carbon content (0.03 per cent or less) containing between 3 and 11 per cent chromium has been measured. Values are given for the mean and true expansion coefficients between room temperature and 800° C.

2. The behavior of these alloys in passing through the alpha-gamma inversion (A_3 point) at a constant rate of heating or cooling has been studied dilatometrically. The transformation temperatures on cooling are very much lower than those observed on heating, an effect that is shown to be related to the rate of transformation of austenite to ferrite. It is shown that this lag can be estimated from the curve giving this rate of transformation as a function of temperature. The data illustrate strikingly that in many cases the use of cooling curves, or of any measurement in which the specimen is cooled, may, and frequently does, lead to large errors. The lag on heating through the inversion is very much smaller.

3. The dilatometer readings show that the rate of transformation of the alloys on cooling is of the same type as the rate for nickel and manganese steels previously discussed by Bain.

4. The limits of the two-phase region of the gamma loop have been tentatively assigned. The shape of the gamma loop is, in accord with expectation, consistent with the change in distribution of chromium between alpha and gamma phases with change of temperature and of total chromium content.

¹⁶ Bain: *Trans. A.I.M.E.* (1932) **100**, 1.

¹⁷ Tammann: *Ztsch. anorg. allgem. Chem.* (1933) **214**, 407.

DISCUSSION

(C. H. Herty, Jr., *presiding*)

G. E. DOAN,* Bethlehem, Pa. (written discussion).—The broadest scientific significance has come to attach itself to the reports issued by the United States Steel Research Laboratory. In just one respect does it seem to me that the present paper may lead to error when viewed from this broad standpoint; namely, the inference on pages 297 and 298 that, since transformations proceed slowly in concentrated solid solution such as 9 per cent chromium austenite, therefore all cooling-curve data and the equilibrium diagrams based upon them are likely to be seriously in error. Since hundreds of equilibrium diagrams now in use are based upon cooling-curve data, the point is an important one.

On page 297 we read: "One example of the usefulness of an estimate of this sort is in indicating the serious errors that may be made in the determination of equilibrium diagrams by any method involving cooling." At the end of this paragraph, the authors conclude: "The only safe way to determine an equilibrium datum is to approach the equilibrium from both sides." As substantiation for these broad claims, the authors cite the case in which a 9 per cent chromium alloy cooled at the rate of 3° per minute yields a transition temperature that is in error by 40° C., and a second case in which the rate of cooling is 0.5° per minute and the error about 20° C. The implication is clearly, although probably not intentionally, made that all equilibrium diagrams based on cooling curves may easily be from 20° to 40° C. in error. This suggestion and the general conclusion drawn from it at the end of the paragraph would certainly fill us with alarm if it were not qualified.

In another type of transition, the liquid-solid transition, cooling-curve methods are commonly used. Under proper conditions there is, of course, the possibility of undercooling. In most cases, this possibility is less than that for solid-solid transitions, and very much less than in the case of solid-solid transitions in a concentrated solid solution. I think without question we may continue to repose considerable trust in the present liquidus curves of most equilibrium diagrams and in the transition temperatures of many solid phases where the concentration of reaction retarding elements is low. Nevertheless, the warning the authors have sounded for the case of solid-solid transitions, especially in the concentrated solid solutions, is both timely and well founded.

J. B. AUSTIN AND R. H. H. PIERCE, JR. (written discussion).—It certainly was not our intention to imply that *all* cooling-curve data are in error by 40° C. or even by 20° C., a fact that we thought we had indicated by saying that serious errors "may be made" rather than that they *are* made. Since, however, there appears to be room for misunderstanding, we are grateful to Dr. Doan for bringing the matter up, so that we can restate our position, which briefly is as follows: Although we do not believe that *all* so-called equilibrium temperatures as taken from cooling curves are in error by 20° C. or more, we do hold that many of them are off by this amount, especially those for the gamma-alpha inversion in the ferrous alloys containing a relatively large concentration of alloying component. An extreme example is found in the alloy containing 13 per cent manganese, which, as a result of studies made with cooling curves, has long been regarded as having a stable, completely austenitic structure down to room temperature. As a matter of fact, this alloy must have an A_3 point somewhere in the neighborhood of 600° C., because a determination of the true

* Associate Professor of Metallurgy, Lehigh University.

equilibrium at 525° C.¹⁸ shows that at this temperature the stable structure contains over 20 per cent of ferrite. Further confirmation of this view is found in the available cooling data for high-chromium and high-nickel alloys, and we suspect that even Dr. Doan would not care to determine the equilibrium in the 18-chromium 8-nickel alloy from a cooling curve.

It is our further contention that all solid-solid transition temperatures derived from cooling curves, even if the concentration of alloying element is low, differ from the true equilibrium temperature, although the difference is often only 4° by 5° C., which is or is not serious, depending upon the individual point of view. Sato's study of the iron-carbon alloys gives the typical behavior of the low-alloy system.

Our statement that "the only safe way to determine an equilibrium datum is to approach the equilibrium from both sides" merely expresses an elementary precaution of practical physical chemistry and is based on general experience. We find it difficult to understand why it should cause anyone to be alarmed.

We agree with Dr. Doan that the possibility of error in observing a solid-liquid transition on cooling is considerably less than in solid-solid inversion, but even here the cooling curve seldom gives reliable data on the true equilibrium, a fact that has long been recognized and generally admitted by those who have studied inorganic equilibria, particularly in silicates. For this reason, and also because of the general difficulty of making precise measurements at high temperatures, we regret that we cannot share his "considerable trust in the present liquidus curves of most equilibrium diagrams."

We feel that Dr. Doan's argument would have been more convincing had he given a few examples of ferrous alloys where true equilibrium temperatures were determined accurately from cooling curves.

¹⁸ See E. C. Bain: On the Rates of Reactions in Solid Steel. *Trans. A.I.M.E.* (1932) **100**, 1; especially Fig. 9.

Dependence of Rate of Transformation of Austenite on Temperature

By J. B. AUSTIN*

(New York Meeting, February, 1935)

It is now well established, chiefly through the work of Davenport and Bain,¹ that the influence of temperature upon the rate of transformation of austenite to ferrite at constant temperature is represented by a curve of the type shown in Fig. 5 on page 295 and the reasons for this general shape have been discussed by them in a qualitative way. Thus, the upper part, or nose, of the curve is the resultant of two factors of which the rate of change with temperature is not the same, and by analogy with other like cases it is almost certain that these factors are: (1) the chemical potential, or driving force, of the transformation, which is zero at the equilibrium temperature and increases rapidly as the temperature falls below this point; and (2) a factor analogous to viscosity, or resistance of the crystal lattice to a change in structure, which also increases as the temperature is lowered. Just below the equilibrium temperature this virtual "viscosity" of the metal is relatively low—that is, the metal offers little resistance to a change in lattice—but the driving force is also small, and the net result is that the reaction proceeds slowly. As the temperature is lowered the magnitude of both factors increases; but at first the driving force increases more rapidly than the resistance and the reaction is observed to proceed more rapidly. At lower temperatures, however, the resistance begins to increase faster than the driving force, and eventually, at the nose of the curve, overbalances it, causing the reaction to proceed more and more slowly thereafter.

This concept is somewhat, though not completely, analogous to that employed in certain electrical cases where the precise factors are known and are separately measurable. The current I (in amperes or coulombs per second) flowing through a given wire is proportional to the impressed potential, or driving force E , and is inversely proportional to the resistance R of the wire; that is, $I = E/R$. Stated in a slightly different way, the time required for one coulomb to pass a given point ($1/I$) is equal to R/E . If the temperature of the whole circuit is changed, the resultant change in $1/I$ will depend on the relative rates of change of R and of E ,

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¹ Davenport and Bain: *Trans. A.I.M.E.* (1930) **90**, 117.

which under certain conditions causes a minimum in $1/I$. This is illustrated in Fig. 1, in which the left-hand side represents the variation with temperature of the resistance of a platinum wire and of an electromotive force not unlike that of certain dry cells. (In this case the driving force and resistance increase with temperature, whereas with the metal both increase with decreasing temperature. However, this is unimportant, since it is the relative change of the two, not their absolute variation,

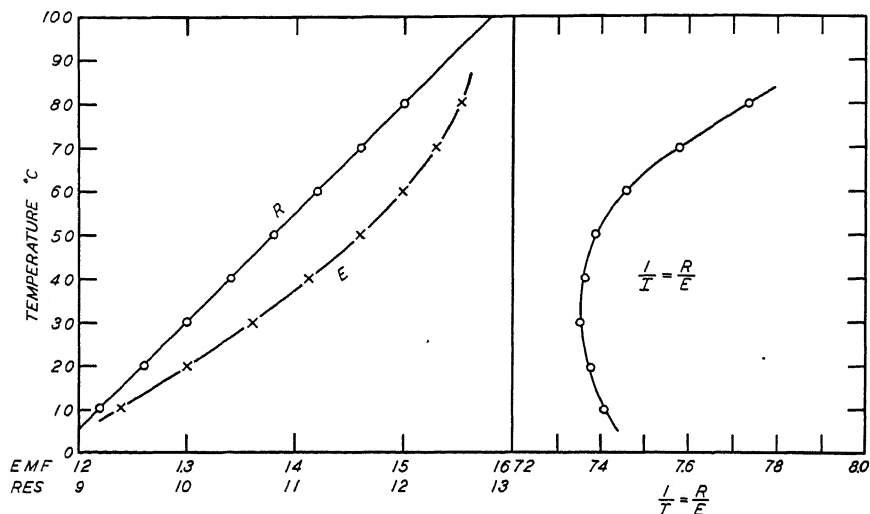


FIG. 1.—CURVES SHOWING TEMPERATURE VARIATION OF RESISTANCE R , ELECTROMOTIVE E AND CURRENT I IN AN ELECTRICAL CIRCUIT.

that counts.) The resultant curve for R/E , derived from these two curves, is plotted on the right-hand side of the figure and shows clearly that the time required for the passage of one coulomb passes through a minimum similar to that observed in the decomposition of austenite.

Such qualitative treatment has been, on the whole, quite satisfactory for most purposes, but there are times when it would be convenient and useful to have these relations expressed in quantitative form. For example, it has been shown² that the lag in the $\alpha - \gamma$ transformation to be expected for any given rate of cooling can be estimated from a curve of the type shown in Fig. 2,^{2a} if such a curve is available; and if some generalized form of equation for the "nose" of the curve could be set up, this lag could be approximated for a great many different experimental conditions from a relatively small number of observations. A semi-quantitative treatment of this problem has been given by Upton,³ but

² Austin and Pierce: page 289, this volume.

^{2a} See also Fig. 5, page 295.

³ Upton: *Trans. Amer. Soc. Metals* (1934) **22**, 690.

since his results cannot be conveniently applied in specific cases an attempt has been made to derive a general expression for this type of curve by a different method.

The "driving force" of the transformation reaction is obviously the chemical potential measured by the free energy change (ΔF) accompanying the transformation. This quantity is most conveniently expressed for the present purpose, not in terms of absolute temperature but in terms of the temperature interval below the equilibrium point; and, in fact, the best way to compare the rate of decomposition of austenite for any two steels is in "corresponding states," that is, when they are both the same interval below their equilibrium temperature, whatever that happens to be; therefore this temperature interval (ΔT) rather than an absolute temperature will be used throughout this discussion.

Strictly speaking, the variation in free energy is different for each composition of metal, but since the heat capacity of iron is little influenced by the addition of small quantities of alloying elements it will be assumed as a first approximation that the change in free energy in the reaction is the same as that for pure iron. The equilibrium temperature for iron alloys, of course, will not be the same as that for pure iron but since we have taken a temperature scale based on the equilibrium temperature, at which ΔF is zero, the alloys are in approximately corresponding states. For alloy systems that show a closed gamma loop, the equilibrium temperatures are taken as the low-temperature boundary of the two-phase region; while for systems in which austenite is stabilized the eutectoid temperature is used. The quantity ΔF is entirely analogous to the function $\psi(T_c - T)$ used by Upton, aside from the fact that he considers it as having a specific value for each metal whereas in the above discussion the values are taken as characteristic of all ferrous alloys in corresponding states.

The numerical data available for ΔF are not very precise, particularly for temperatures close to the equilibrium point, but a satisfactory representation, at least for values of ΔT as great as 200° C. is obtained by assuming that ΔF varies as the cube of ΔT ; and the equation

$$\text{austenite} \rightarrow \text{ferrite}; \Delta F = -25 \times 10^{-6} \Delta T^3 \quad [1]$$

although to a large extent arbitrary, is not inconsistent with the rather unsatisfactory data for pure iron (see Table 1). In this expression ΔF is the free energy change in calories accompanying the transformation of 1-gram atom (55.84 grams) of austenite to ferrite, or within the limit of accuracy to ferrite and cementite, and ΔT is the interval below the equilibrium temperature taken as positive. Since, other things being equal, the time t required to produce a measurable quantity of ferrite,

which is taken as the time required for the reaction to start, is inversely proportional to the driving force, we get

$$t = +a/\Delta T^3 \quad [2]$$

where the constant a is the proportionality factor.

The second factor, virtual "viscosity" or resistance, is, on the other hand, not the same for all iron alloys but, judging by the shape of the decomposition curve and its observed shift with change in composition,

TABLE 1.—*Temperature Variation of Free Energy Change in Transformation of Austenite to Ferrite*

| Temperature Interval Below Equilibrium Point T°C. | Free Energy Change ΔF Cal per Gram Atom | |
|---|--|----------------------------|
| | Based on Experimental Data for Pure Iron ^a | Calculated from Equation 1 |
| 0 | 0 | 0 |
| 50 | — 7 | — 3 1 |
| 100 | — 25 | — 25 |
| 150 | — 47 | — 34 |
| 200 | — 85 | —100 |
| 250 | —116 | —156 |

^a The values for ΔF for pure iron are not very accurate, since they are derived by taking small differences between large numbers. The above values are based primarily on the equation given by Chipman (*Jnl. Ind. & Eng. Chem.* (1933) **25**, 319, eq. 2) but have been adjusted to be consistent with $\Delta F_{900} = 0$.

must vary enormously with both temperature and composition, a conclusion that is not unreasonable since the viscosity of many substances is known to do just that. (It should be noted here that this factor is analogous to Upton's function $\phi(T)$ except that he considers it a general function applicable to all metals rather than a specific property as has been done in this discussion). As a first approximation it has been assumed that the "viscosity" is proportional to $e^{ca\Delta t}$ so that the contribution of this factor to the time required to produce a detectable amount of ferrite (time for the reaction to start) is:

$$t = be^{ca\Delta t} \quad [3]$$

Combining equations 2 and 3, we obtain

$$t = \frac{Ke^{ca\Delta t}}{\Delta T^3} \quad [4]$$

where $K = a \times b$.

It is interesting to note in this connection that in order to make equation 4 dimensionally correct the term $(Ke^{ca\Delta t})$ must have the dimen-

sions of viscosity. Equation 4 as it stands contains two arbitrary constants K and c , to one of which can, however, be assigned a general value. Differentiating (4) with respect to ΔT we have:

$$\frac{dt}{d(\Delta T)} = -\frac{3K}{\Delta T^4} e^{c\Delta T} + \frac{cKe^{c\Delta T}}{\Delta T^3} \quad [5]$$

At the point of the nose, that is, when t is a minimum, $dt/d\Delta T = 0$, and therefore

$$c = 3/\Delta T_{\min} \quad [6]$$

or the constant c is equal to 3 divided by ΔT_{\min} , the temperature interval below the equilibrium temperature at which t is a minimum. It is a striking fact that in practically every steel for which we have been able to get satisfactory data, the temperature at which the decomposition of austenite is fastest is approximately 150°C. below the respective eutectoid temperatures. If, therefore, we set $\Delta T_{\min} = 150$, that is, $c = 0.02$, and write

$$t = \frac{+Ke^{+0.02\Delta T}}{\Delta T^3} \quad [7]$$

there is obtained a general expression fitting the experimental data for a number of steels as well as can be expected in view of the simplifying assumptions made in its derivation and of the difficulty involved in making precise measurements of the rate of transformation when t is close to its minimum. The accuracy with which equation 7 reproduces the experimental results is illustrated in Fig. 2, which compares the observed and calculated values for two alloys of widely different composition. The failure of the calculated curve to swing back as rapidly below the nose as does the experimental curve is due to the fact that as the temperature goes farther and farther below the equilibrium temperature ΔF does not continue to increase as the cube of ΔT (Table 1) but as some smaller power, thereby making the denominator of equation 7 too large and the calculated value of t too small. A more complicated expression, which will give a closer fit, can easily be derived but would hardly be worth while until more steels have been studied carefully.

The general shifting of the curve with composition is taken care of by the constant K , which varies enormously, as, for instance, about a hundredfold in the two cases shown in Fig. 3. If even a single point on the curve is known, K can be evaluated and the upper part of the curve can be plotted with an accuracy sufficient for some purposes, such as the one mentioned in the introduction. It should be noted, however, that because of the form of the equation it fits the observations best if K is determined from a point somewhere near the nose, in about the position

of the points selected in Fig. 2. If K is evaluated from a point for which t is very large or very small the approximation is usually not so good.

If data are available for a series of alloys or steels in which the composition is varied in a regular way, a curve of K versus composition can be constructed from which a value of K can be read off for any intermediate composition for which no data exist; and in this way it may be possible to construct for such an alloy a rate curve that will be satisfactory for many purposes, such as calculating the lag in the A_3 transformation on cooling at various rates.

The agreement between the calculated and observed curves in Fig. 2, while gratifying as a check on the general validity of the concept and while

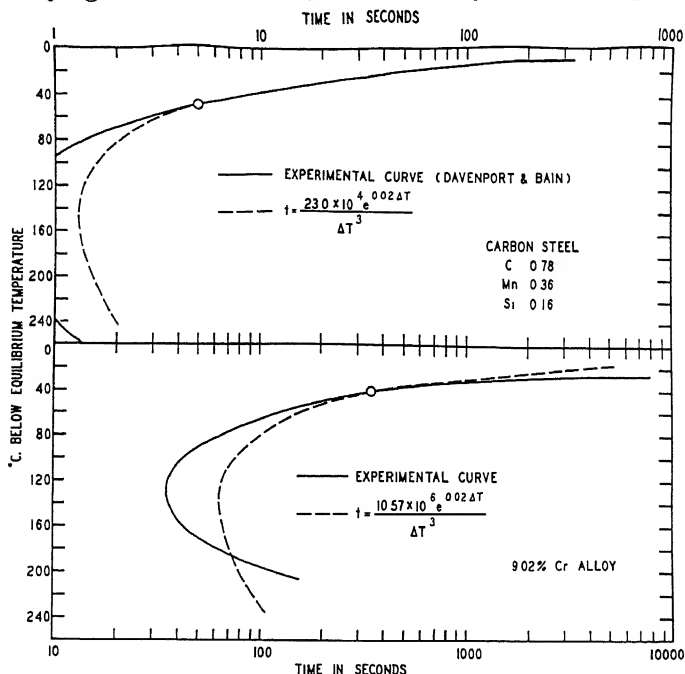


FIG. 2.—COMPARISON OF CURVES CALCULATED FROM EQUATION 7 (DASHED LINES) WITH THE EXPERIMENTAL DATA (SOLID LINES).

Note that scale of lower block starts at 10 whereas upper one begins at 1.

Circles represent points from which K was determined.

sufficient to show the usefulness of the calculated curve for some purposes, is not good enough as it stands to permit equation 7 to be applied to all cases. For example, the difference between the two curves at the nose would in practice correspond to a difference in hardenability much greater than is allowable in good designing, and the generalized equation should not be used in applications of this sort. Moreover, while there are indications that equation 4 will hold for many reactions, equation 7 must be used with caution because the constant 0.02 is not rigorously general, but is valid only for a number of cases of the transformation of

austenite to ferrite, or to ferrite and cementite or some other carbide. It does not apply to the transformation of austenite to martensite nor to the formation of austenite from ferrite. The general method used here should be applicable in these cases, and the form of the equation may be the same, but the constants c and K must be obtained from experimental observations. It is interesting to note, in this connection, that there is a marked difference in the "viscosity" or resistance of change of the lattice for the reactions $\alpha \rightarrow \gamma$ and $\gamma \rightarrow \alpha$. It is well known that the formation of austenite from ferrite in general occurs much more rapidly than the reverse reaction, which has been discussed here, and since the change of ΔF with temperature above the equilibrium point is very nearly the same as below, most of the difference in rates must be due to the difference in the ease with which the lattice is shifted. Just why the change from ferrite to austenite should be so much more rapid is not clear at present. It may possibly be connected with the ease of converting a body-centered cubic lattice to a face-centered one as compared to the reverse transformation, but in view of the fact that in general transformations on heating, including melting, show a much smaller tendency to lag than do those on cooling it seems likely that the cause lies in something more fundamental.

Thus far this discussion has been limited to the start of the transformation and has not considered what happens during the course of the reaction, which appears to be a more complicated problem. Thus, it is now established that the reaction once started proceeds with increasing rapidity, implying a correspondingly rapid change in the virtual "viscosity," a phenomenon which in many respects resembles the autocatalysis observed in other chemical reactions. The autocatalytic behavior seems, however, to appear only in the early stages of the transformation,⁴ since, as Bain has pointed out, the rate of reaction after a relatively short time follows the established course of a unimolecular reaction.

For the benefit of those who may wish to use these equations, values of e^z are given in the standard handbooks and tables, such as Marks' Mechanical Engineers Handbook or the Chemical Rubber Company's Handbook of Chemistry and Physics.

APPENDIX

The above work had already been completed at the time that Upton⁵ advanced his belief that the temperature lag in the alpha-gamma transformation in iron and steel varies as the cube root of the rate of heating and cooling. At first glance the fact that equation 7 contains the term ΔT^3 appeared to support this view, especially since the experimental

⁴ Bain: *Trans. A.I.M.E.* (1932) 100, 1.

⁵ Upton: Reference of footnote 3.

factor $e^{0.02\Delta T}$ is approximately equal to unity for the relatively small values of ΔT considered by Upton and therefore can be neglected in comparison with ΔT^3 . On closer examination, however, it was found that this first impression was false, as is evident from the following reasoning:

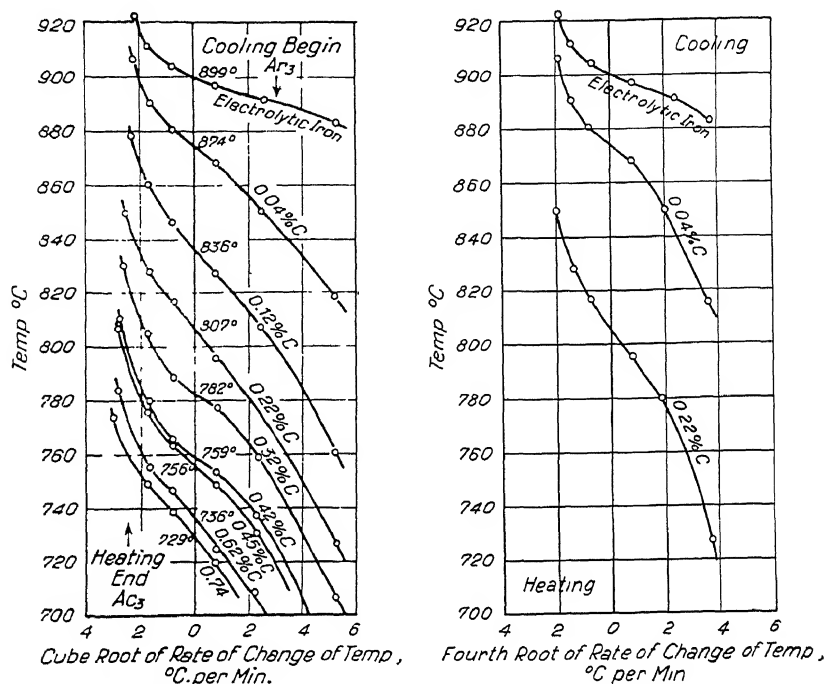


FIG. 3.—SATO'S DATA ON EFFECT OF RATE OF HEATING OR COOLING ON TRANSFORMATION TEMPERATURE OF HYPOEUTECTOID STEELS.

Plotted (a) using cube root of rate of temperature change (Upton) and (b) using fourth root instead of cube root.

The time t in equation 7, that is, the time required for the transformation to start, is related to the temperature lag (ΔT) and to the rate of cooling R by the relation

$$tR = \Delta T$$

Putting this value for t in equation 7, gives:

$$\Delta T/R = \frac{Ke^{0.02\Delta T}}{\Delta T^3}$$

or setting the exponential factor equal to one we have the following series of approximate equations:

$$\Delta T/R = K/\Delta T^3$$

or

$$\Delta T^4 = KR$$

and

$$\Delta T = \sqrt[4]{KR}$$

In other words, the temperature lag is proportional to the fourth root of the rate of cooling. This is admittedly an approximation, since the choice of the cubic exponent for ΔT is, in view of the uncertainties in the data on ΔF , somewhat arbitrary. Had ΔT^2 been taken instead of ΔT^3 in equation 2 the Upton relation would have been obtained. On the other hand, as Schwartz⁶ pointed out in a discussion of Upton's work, the curves given by Upton do not follow the cube-root relation with any great accuracy, and it seemed likely that the fourth-root relation might do just as well. Accordingly the data of Sato,⁷ from which Upton deduced the cube-root relation, were plotted using the fourth root of the rate of change of temperature instead of the cube root. The results are compared in Fig. 3 with Upton's cube-root curves as taken from his paper. So far as the author can see there is little difference between the two and it is concluded that neither relation is of any great value, aside from being a convenient method of extrapolating to zero rate, since they are both only poor approximations. About all that can be said is that they seem to be somewhat better for cooling than for heating, which is not surprising since equation 7, from which the fourth-root relation is derived, is admittedly not valid for the alpha-gamma transformation on heating.

SUMMARY

The curve representing the variation of the rate of decomposition of austenite with temperature can be represented with fair accuracy by the equation

$$t = \frac{Ke^{0.02\Delta T}}{\Delta T^3}$$

where t is the time required for the reaction to start, K is an arbitrary constant and ΔT is the temperature interval below the equilibrium critical point.

⁶ Schwartz: *Trans. Amer. Soc. Metals* (1934) **22**, 719.

⁷ Sato: *Tech. Repts. Tôhoku Imp. Univ.* (1928) **8**, 27.

Graphite in Low-carbon Steel

By A. B. KINZEL,* MEMBER, A.I.M.E., AND R. W. MOORE†

(New York Meeting, October, 1934)

ALTHOUGH the iron-carbon diagram has undergone many changes in the last 20 years, the region below the eutectoid line and up to approximately 1.7 per cent carbon has been little affected. This region is generally considered to consist of cementite and ferrite. Graphite has been noted occasionally in the hypereutectoid steel region, and the ready formation of graphite nodules in malleable cast iron is a phenomenon difficult to interpret in the light of cementite, supposedly stable at sub-eutectoid temperatures. In this case the graphite formation has been partly explained by the presence of silicon, and many have believed that silicon acts to change the stable state rather than to accelerate reactions so as to arrive at the stable state in a briefer period of time. Consideration of this phenomenon indicates that cementite is not the stable phase in the temperature composition zone referred to.

In the course of examining a low-carbon steel tube taken from a petroleum cracking still, which had been in service for approximately three years at temperatures somewhat below the eutectoid temperature, observations were made that shed light on this entire subject. The tube in question analyzed: C, 0.15 per cent; Mn, 0.49; Si, 0.02; S, 0.023; P, 0.015. The microstructure of the tube after service is shown in Figs. 1 and 2. From these it is evident that cementite as such is absent, and that in its place nodular graphite has been formed. In order to check this observation further, samples taken from the tube were heated at 850° C. for varying periods of time. The small samples were put into a large hot furnace, and the total time is recorded. The structure of the sample after 5 min. at 850° C. is shown in Figs. 3 and 4, and the nest of pearlite surrounding the graphite nodules is most satisfactory evidence of the character of the nodules. As the length of time of heating at this temperature increases, the pearlitic zone increases, with final restoration

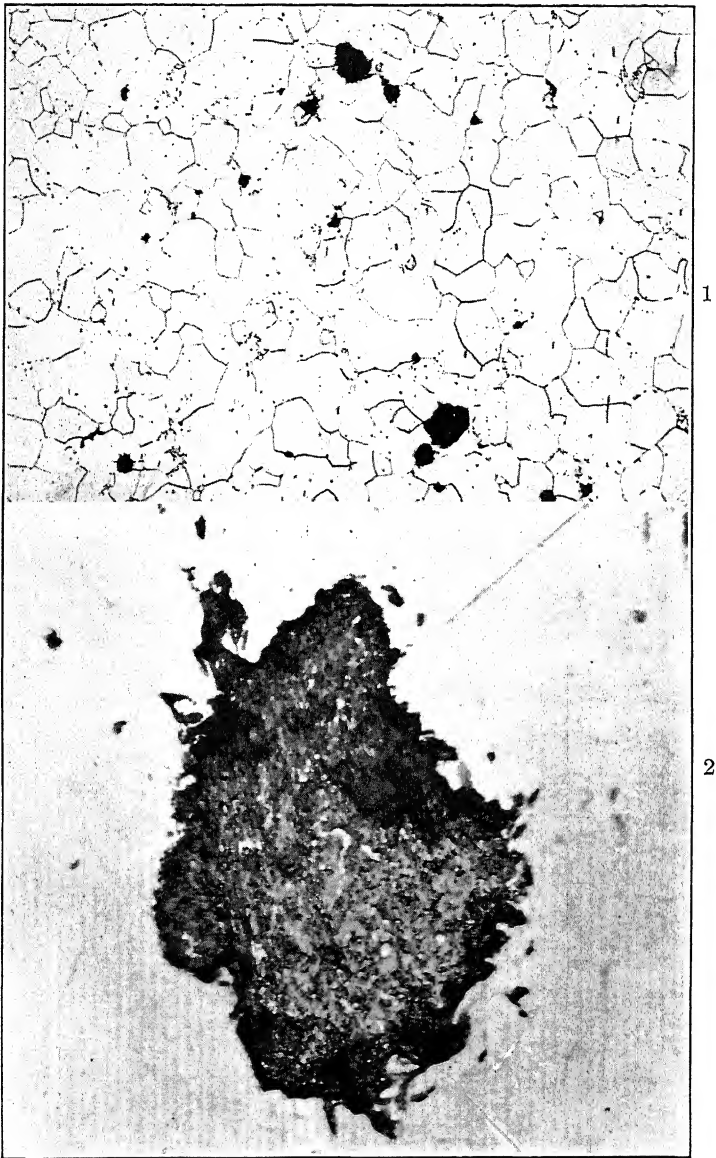
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¹This analysis was carried out after service and corresponds to the purchase specification.

of the pearlitic structure as we would expect it to exist in normalized steel of this carbon content. This is illustrated in Figs. 5 to 9. In the



FIGS. 1 AND 2.—MICROSTRUCTURE OF TUBE AFTER SERVICE, AS RECEIVED.
Samples taken from tube about six feet from firing end of still.
Fig. 1, $\times 100$. Fig. 2, $\times 750$.

course of examining a number of tubes that had had various lengths of service, it was possible to find spheroidized structures, and spheroidized

and partly graphitized structures. This is in agreement with the general concept of the mechanism of graphite formation. It should be mentioned

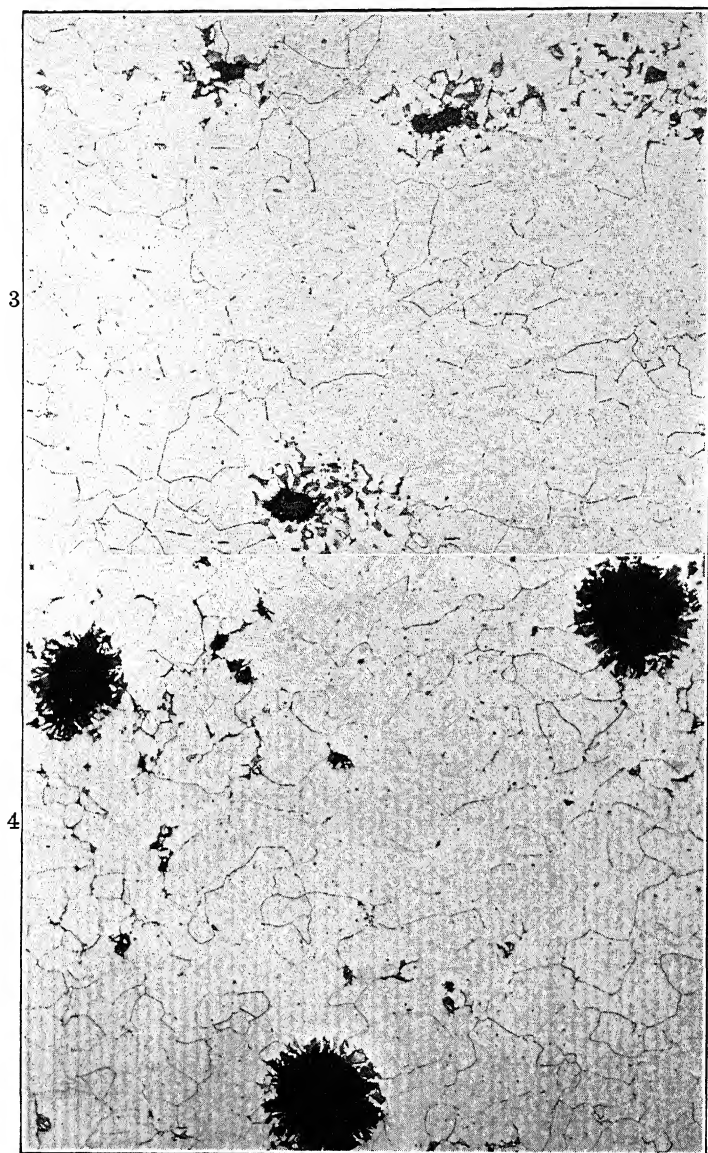


FIG. 3.—MICROSTRUCTURE OF SAMPLE AFTER 5 MINUTES AT 850° C. $\times 100$.
FIG. 4.—SAME AS FIG. 3.

that extreme difficulty was encountered in preparing the samples so as to retain the graphite nodules, and that Mr. J. Vilella should be credited for the excellent photomicrographs.

The evidence given here speaks for itself. It is particularly striking in view of the fact that to the best of our knowledge graphite has never

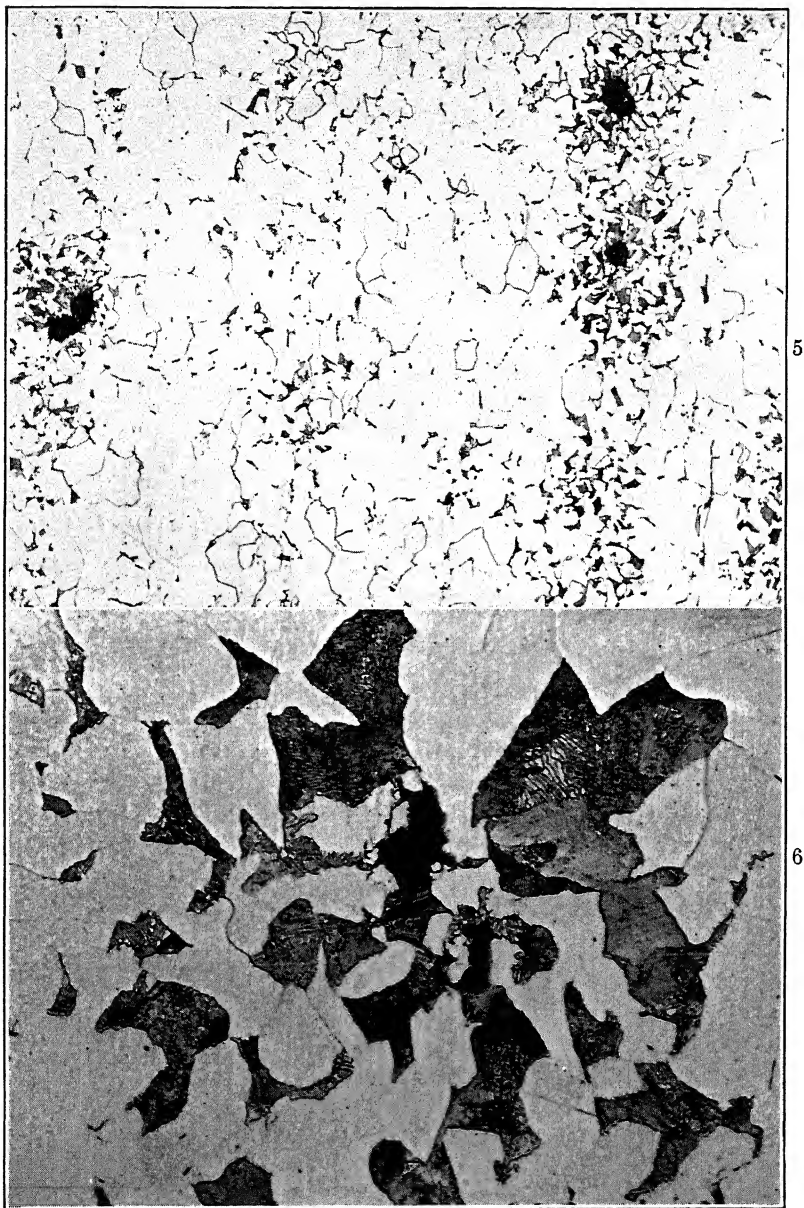


FIG. 5.—MICROSTRUCTURE OF SAMPLE AFTER 10 MINUTES AT 850° C. $\times 100$.

FIG. 6.—MICROSTRUCTURE OF SAMPLE AFTER 10 MINUTES AT 850° C. $\times 750$.

before been observed in low-carbon steel. It is also most gratifying because it is a result that had been predicted from general theoretical

considerations. The evidence leads to the definite conclusion that the truly stable phase in the iron-carbon system at temperatures below the

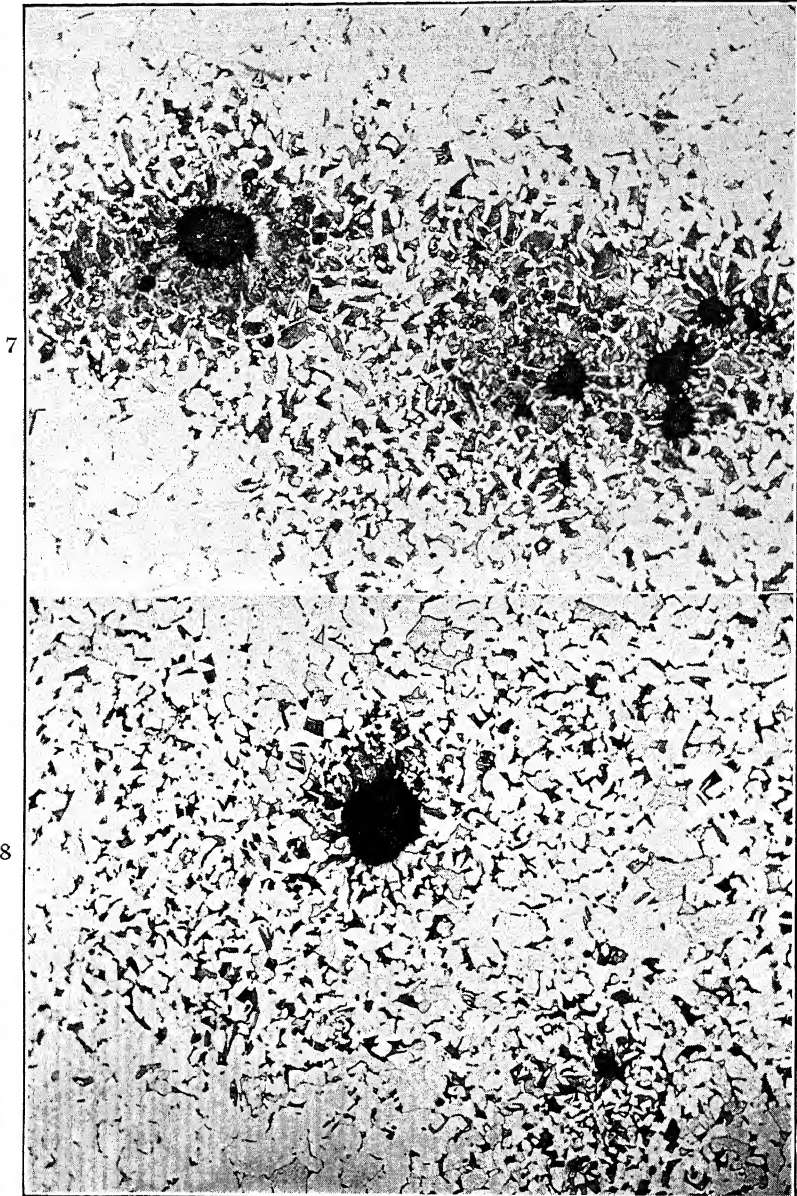


FIG. 7.—MICROSTRUCTURE OF SAMPLE AFTER 15 MINUTES AT 850° C. $\times 100$.

FIG. 8.—MICROSTRUCTURE OF SAMPLE AFTER 30 MINUTES AT 850° C. $\times 100$.

eutectoid temperature is graphite rather than cementite. This conclusion is drawn in the light of the impurities contained in the sample in

question, and may require modification accordingly. However, the low silicon content, together with the low values for the other elements,

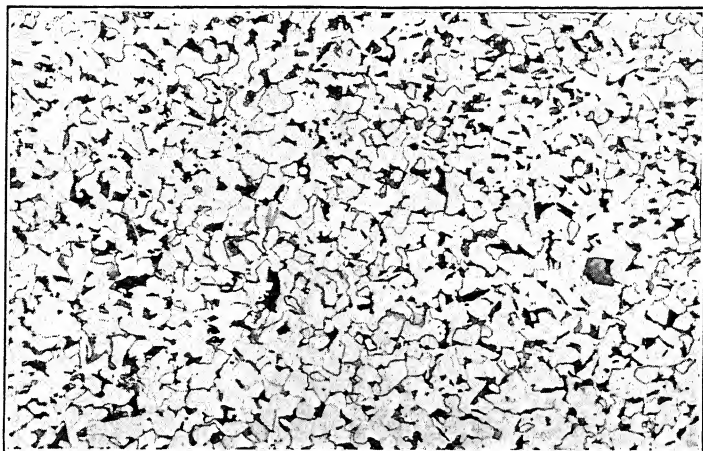


FIG. 9.—MICROSTRUCTURE OF SAMPLE AFTER 120 MINUTES AT 850° C. $\times 100$.

makes it highly probable that the conclusion is valid for the pure iron-carbon system.

DISCUSSION

(Francis B. Foley presiding)

H. A. SCHWARTZ,* Cleveland, Ohio (written discussion).—This paper furnishes welcome confirmation of the fact that iron carbide is unstable even in the hypoeutectoid steels and will graphitize if given an opportunity. It seems unfortunate that the authors should say at the very beginning of their paper that cementite is “supposedly stable at subeutectoid temperatures.” So far as the writer is aware all observers that have studied the problem have considered it to be metastable. Such discussion as there has been in the past suggesting that cementite is ever stable was in the direction of proving that this compound might be stable at some very high temperature, say, perhaps 900° or 1000° C. or even higher, but metastable at all lower temperatures.

The authors seem well aware of these facts for at the bottom of page 321 they refer to the fact that this result had been predicted from general theoretical considerations. Alloys of this kind are extremely slow to graphitize, possibly among other reasons because of the difficulty of establishing centers of crystallization for carbon.

A particle of cementite enclosed in a mass of ferrite saturated with cementite does not in any way differ from a particle of cementite in any other environment. If the compound is metastable it will be metastable in any alloy in which cementite exists as such. The authors rightly cite the graphitization of what would otherwise be pearlite in the second stage of malleable annealing; in that case graphitization is relatively rapid, of course, because there are many centers of graphitization. There comes a time when the remaining cementite corresponds to any chosen carbon content. This content may be chosen just as low as one wishes provided it is beyond the amount

* Manager of Research, National Malleable and Steel Castings Co.

that will dissolve in ferrite. Every malleable casting therefore has had at some time 0.15 carbon as cementite and graphitized further just as did the hypoeutectoid tube examined by the authors. The phenomenon is not more frequently encountered because specimens of low-carbon steel that have been heated in this temperature for several years are not frequently available for observation.

The metastability of the iron-cementite system is represented in the double iron-carbon diagram by the location of A_1 stable above A_1 metastable. The solubility of cementite and of carbon in ferrite is tacitly taken as zero as the diagram is usually drawn. These solubilities are so small that the line representing them apparently coincides with the ordinate at zero carbon if the diagram is constructed on a scale suitable for showing most of the other equilibria. As a matter of fact, the diagram probably has two lines marking this solubility and representing slightly increased solubility with increase of temperature. The line representing the solubility of graphite should be to the left of the line showing the solubility of cementite, although no one has actually plotted its locus. The fact that the orthodox iron-carbon diagram does not recognize this difference is not so much an error of intent as due to the lack of "resolving power" of the human eye.

F. B. FOLEY, * Philadelphia, Pa.—I suppose most of us are aware of many instances of the formation of carbide at these temperatures at which we now have a striking example of graphitization of cementite.

It was not so many years ago that Carpenter produced from iron and carbon a constituent he called, I think, the X constituent. I recall very clearly the instance of a piece of pure iron suspended in the blast-furnace downcomer, where the temperature was certainly not above the critical temperature of steel and which ultimately reverted to pure cementite in a matter of months. That brings up the thought that it was 10 or 15 years ago that I had occasion to examine a piece from the bottom of a coking still. This piece had been obtained when a workman, in trying to straighten out a bulge in the bottom of the still, found the piece dropped out like a piece of glass.

On examining that piece, I found pure cementite on the side in contact with the coke in the bottom of the still. The temperature probably was not above the critical temperature of steel because the bottom of this type of still is watched for the appearance even of a red color. There still is some chance that inadvertently the locality of this particular specimen might have been heated to above its critical temperature. But, the other cases seem to be very strong.

We have before us today a remarkable instance of graphitization. I think it is the only one where there is as little as 0.05 of silicon present in the steel. I believe Charpy did a great deal of work with graphitizing low-carbon steels with high silicon content.

J. A. MATHEWS, † New York, N.Y.—Volumes and volumes have been written on iron and graphite in pig iron, and cast and malleable iron, but the subject of graphiting of steels seems to have been neglected. Prof. William Campbell published some work on it in the A.S.T.M. many years ago. He ascribed it to an overheating during the earlier processes of working down the steel.

About 1907 we had a customer who had been buying a high-carbon tool steel from us for a good many years. The company decided to put in its own annealing furnace, and ruined the steel. The company blamed our steel, and we blamed the company for not knowing how to anneal.

* Superintendent of Research. The Midvale Co.

† Vice President, Crucible Steel Co. of America. Died Jan. 11, 1935.

I started some work at that time. I found there was a tremendous difference in the ease with which different high-carbon steels could be graphitized. It was not proportional to the carbon content, by any means. We found some with 1.70 carbon that was hard to graphitize by long, low annealing and some with 1.10 and 1.20 that could be readily graphitized. The steels included our own and many foreign and domestic brands.

My "boss" at that time seemed to have the same idea as Professor Campbell, that graphiting was due to abuse during the cogging or rolling operation. I told him I would produce it in the hammered billet. It had had no rolling, and by annealing we produced it in the billet. Not satisfied with that, I promised him I would produce it in the ingot. We used to knock off the crucible-steel ingot tops for the purpose of estimating the carbon, and by long annealing we obtained from 0.10 or 0.15 graphite in ingot metal. We separated and analyzed it quantitatively. The temperatures at which I produced it were lower than those mentioned by Dr. Kinzel.

An electric tube furnace that would barely reach the decalescence was used. I put the end of a bar of steel in the middle of the furnace and used a pyrometer that would slip up and down to measure the temperatures at various points. After long annealing, I would quench. There would be a sharp bend indicating the portion of the bar that had been above the decalescence, and by drilling from there on back toward the cold end, I found graphite present in decreasing quantities down to very low annealing temperatures, as low as 450° C. I have often wondered why the whole question of the production of graphite in carbon steels has not received more attention. It may be associated with steel-melting practices and many other things besides mere composition. Silicon tends to promote it, and nickel tends to promote it in the high-carbon steels, while chrome and manganese are inhibitors. I never have seen it in a steel as low in carbon as Mr. Kinzel describes.

I think this is an ideal investigation for somebody in a college laboratory, to determine the conditions under which carbon steel graphitizes, and thus complete our knowledge on the subject.

R. W. MOORE.—There may be some connection between this paper and that on Use of Reflected Polarized Light in the Study of Inclusions in Metals, by S. L. Hoyt and M. A. Scheil².

When the tube from which the graphitized steel was obtained failed a crack was formed running parallel to the length of the tube. Adjacent to the crack were a number of inclusions, which we assumed to be oxide inclusions. An examination of the inclusions was made with polarized light in a manner somewhat similar to that mentioned by Dr. Hoyt. We found that some of them showed the anisotropism he mentions. One in particular gave the appearance of a conchoidal fracture when viewed in the microscope under ordinary light. There was a series of parallel lines which were cut through by other lines of demarcation running somewhat perpendicular to them. These lines of demarcation set off certain variations in the gray color of the inclusion. When viewed with polarized light, these areas would become alternately light and dark as the piece was rotated.

We have not determined the nature of these inclusions. They do not show any test for sulfide nor do they respond to the tests commonly used by mineralogists for identifying the various iron oxides. We do not believe them to be silicate inclusions. Perhaps the material presented by Hoyt and Scheil may help in the further identification of these inclusions.

J. A. MATHEWS.—In high-carbon steels, we have found that the graphite up to about the eutectic composition seems to go back into solution very readily just by

² Page 405, this volume.

ordinary heating and quenching. The steel becomes very hard, but the excess remains as free graphite and is difficult to get back into solution. That excess graphite remaining in the hardened steel gives it the characteristic dry, stone fracture with which we are familiar.

In the ordinary practice of cementation of wrought-iron bars, such as was carried on in the Sheffield furnaces and in this country as well, it was well recognized that to produce cemented bar above eutectic carbon the temperature had to be above 900° C. If cementation took place much below that temperature, only the regular amount of the eutectic carbon would be absorbed.

A. B. KINZEL.—Mr. Schwartz is unquestionably one of those who have always labeled the portion of the diagram in question as metastable. This, however, does not affect the opening remark of the paper that the portion of the diagram in question is generally looked upon as containing stable cementite.

Specimens taken from the tube showing the graphitized structure, but at a point at which a slightly lower temperature existed, showed definitely a partly spheroidized and graphitized condition, showing that the change takes place by spheroidization of pearlite and graphitization of the spheroids. The argument taken from the behavior of malleable castings is not inconsistent with that given here, but it is less applicable to the iron-carbon diagram because of the presence of silicon.

It should be pointed out particularly that no lower limit has been set to the zone corresponding to equilibrium between graphite and cementite. Graphite is produced just below the eutectoid temperature. How much below the eutectoid temperature this condition holds is another question, and one may assume that the condition holds down to room temperature, but this is purely an assumption.

Dr. Mathews' remarks are particularly appreciated and we welcome his contributory evidence in connection with the high-carbon steels. Dr. Mathews' point that this is an excellent starting point for further investigation by some college laboratory or other institution interested in the mechanism and theory involved is to be particularly emphasized. Dr. Moore will be glad to furnish sufficient amounts of material for such further investigation. Dr. Mathews' discussion of the temperature necessary for resolution of the graphite seems to be entirely consistent with the conception of the A_{cm} line, but this is a point that is too often missed.

F. B. FOLEY.—The temperature was not mentioned. Have the authors any idea what temperature this tube actually attained?

R. W. MOORE.—We cannot state exactly the temperature of the metal in these tubes. The conditions of operation can be described and a rough conclusion drawn regarding the temperature. The still from which this tube was removed is known as a DeFlorez cracking still. In cross-section it is a large cylinder in which there is a double tank of vertical tubes about 35 ft. long. At the top of the still is a bank of tubes running horizontally, known as the preheating tubes. Oil in passing through these tubes is warmed up to about 700° F., and from them it passes into one of the vertical tubes in the first quadrant, it passes from one vertical tube to its next adjacent tube, and so on around the furnace.

The thermocouples for measuring the temperature in the still are about 5 to 8 ft. down from the horizontal bank of preheating tubes. These thermocouples register between 1500° and 1600° F. The failure took place about 5 or 6 ft. from the bottom of the furnace, or from the bottom of the tube. Oil as it comes from the preheater goes into the first vertical tube at about 700° F. As it passes on around through the vertical tubes it becomes hotter and finally leaves the furnace at about 1000° F. The tube that failed was about halfway around the bank of vertical tubes. With these

facts and figures in mind and a furnace temperature of about 1600° F., a rough conclusion may be drawn regarding the possible temperature of the metal of the tube.

A. B. KINZEL.—Visual observation indicates that the temperature in question is about 600° C.

F. B. FOLEY.—The temperature is very important because the recent work has shown the Ae point in carbon steels to be 663° F. (1228° F.), which is well below what we have commonly taken it to be. We assume, I think, 1340° F. (726° C.) or 1350° F. (734° C.) as being the Ac₁ of carbon steel.

The question that Dr. Mehl's paper suggested³, as to whether the formation of cementite or of ferrite occurs first in cooling austenite may have a bearing on the question. Might it not be that these tubes were at a temperature where the carbon was precipitated from the austenite but had not formed cementite and that the graphitization is the result of the agglomeration of these particles of carbon as they formed. In other words, that the temperature is not below the critical temperature but actually in it. This might account for graphitization.

A. B. KINZEL.—I do not believe that is possible, in view of the fact that we had the cementite, as such, present along with the graphite in many instances.

F. B. FOLEY.—Can you not imagine that with a slight switch of temperature one way or the other, certain parts were forming cementite and others graphite?

A. B. KINZEL.—It is difficult to imagine them in the same micrographic area. It is highly improbable that such temperature fluctuations could occur.

F. B. FOLEY.—The temperature ought to be more definitely fixed. It is too near a critical zone.

A. B. KINZEL.—The coexistence of cementite and graphite in an area of microscopic dimensions precludes that argument.

A. HAYES,* Middletown, Ohio.—Dr. H. L. Maxwell, in my laboratory at Iowa State, along about 1926 made an equilibrium study of ferrite and cementite in the form of pearlite, with the gases CO and CO₂, from which he calculated heats and free energies of formation of cementite from ferrite and carbon at temperatures of 650° and 700° C. I do not recollect the exact value of that decrease, but I am sure that the free energy increase that he obtained at 650° indicated that metastability was greater at 650° than at 700°. This indicates a decrease of metastability at 700° over that at 650°. An extrapolation of the data indicated that cementite in contact with ferrite ought to become stable at about 800° C. Of course, that is above the temperature where ferrite and cementite would be a stable phase. But, extrapolating those same two values downward would indicate that cementite in contact with ferrite would become more metastable as the temperature was lower, which is all in fine confirmation of what Dr. Kinzel has said.

The explanation of the effect of silicon that I have always liked to resort to is this: If we prepare cementite by electrolytic solution of ferrite away from the cementite in low silicon-bearing materials (up to one per cent), we find no silicon in the cementite. In other words, silicon is readily soluble in the ferrite or the austenite, as the case may be, and does not have a tendency to associate itself with the cementite. Its solution in the austenite in one instance, or in the ferrite in the other, decreases the

³ Page 330, this volume.

* Director Research Laboratories, American Rolling Mill Co.

escaping tendency of ferrite to carbide, or, in other words, it makes it easier for iron to escape from carbide into ferrite, thus increasing the metastability of carbide.

The thing that surprises me about the results that Dr. Kinzel has obtained is that just the reverse of those behaviors is true of manganese; which is, we find manganese closely associated with the cementite when we prepare cementite from iron-carbon alloys, indicating that it associates itself much more readily with the carbide than it does with the ferrite or the austenite. In other words, it has a tendency to stabilize the cementite, and yet, Dr. Kinzel finds this tube has graphitized in the presence of some 0.49 per cent of manganese.

It seems to me that it would be extremely important to know the condition of structure of that tube while it was in service and before it failed and was brought under metallurgical study. I would not be surprised at some unusual effect, possibly, of the highly reducing conditions that come from contact with the decomposition products of cracked oil.

R. F. MEHL,* Pittsburgh, Pa.—I do not know whether I understood our chairman's remark correctly, but the temperature of 600° approximated is certainly far below the A_1 temperature. Our own determinations made during the last year on the A_1 temperature for the purest iron-carbon alloys indicate, on sample after sample, a temperature of 720°, about plus or minus 1° C. The effects of manganese and silicon in displacing this temperature are known and could not in the percentages present reduce A_1 to 600° C. This graphitization definitely must have taken place below A_1 .

R. W. MOORE.—It might also be added that tubes in the vicinity of the one of which we have been speaking fail quite frequently and that the type of splitting and metal structures found are always the same. Failure does not occur very frequently in the first quadrant of the vertical tubes. When such failures do occur in the first quadrant, they are of the type more common in cracking stills in which a bulging occurs before the final failure. The metal structures encountered are of a partially spheroidized nature. There is very little coke deposit found in the first quadrant tubes, a slight deposit about halfway around, and a heavy deposit in the last quadrant, which is difficult to clean out. We have not experienced any failures in the last quadrant of the furnace.

A. B. KINZEL.—The matter of possible effect of gases that Dr. Hayes raised is one that has given us some thought. Any such effect would probably be reflected in a change in carbon content. That is, gases would carburize or would decarburize; as neither of these effects was present we believe that the probabilities are that the atmosphere has nothing to do with the case.

A. SAUVEUR,† Cambridge, Mass. (written discussion).—Has not the belief that graphite rather than cementite represents stable equilibrium been the prevalent one for many years? I certainly always have entertained it. As early as 1912, I expressed it in the first edition of my book on the Metallography of Iron and Steel (p. 22, lesson XII), where I represented final equilibrium by a graphite particle embedded in ferrite. The graphitizing of cementite slightly below the eutectoid temperature can be accomplished in all steels regardless of their carbon content. Of course, the less carbon present, the longer the time required. It may take months or possibly

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† Professor of Metallurgy, Harvard University.

years to graphitize the few cementite lamellae present in very low-carbon steel, whereas the graphitizing of eutectoid steel may be completed in a few days. In Fig. 10 is shown the complete graphitizing of a steel containing 0.90 per cent carbon after quenching from 900° C. followed by heating to 670° C. for 170 hours.

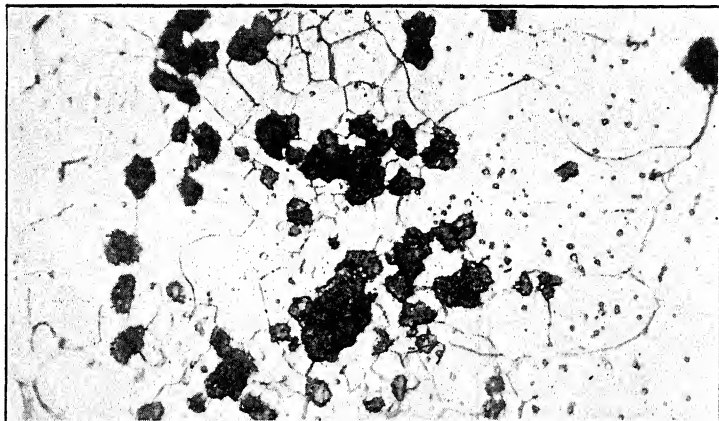


FIG. 10.

A. B. KINZEL.—Dr. Sauveur's illustration is distinctly to the point and serves to further emphasize the validity of the conclusions drawn in our paper. That many of us believed that graphite was a stable phase in the subeutectoid zone of the iron-carbide system cannot be questioned, as this is really the most logical assumption to make. The question has always been clouded, however, by the presence of appreciable quantities of silicon in the ferrite containing the graphite, and we believe the work herein reported is unique in that the silicon is extremely low.

Orientation of Ferrite in Pearlite

By ROBERT F. MEHL,* MEMBER A.I.M.E., AND DANA W. SMITH†

(New York Meeting, October, 1934)

It has been shown by numerous studies that the orientations of new metal crystals are determined by the orientations of the crystals in the original matrix, whether these new crystals are formed by recrystallization, by precipitation from solid solutions, or by transitions in the solid state. The orientations of crystals formed by recrystallization of cold-worked metals that bear preferred orientations are occasionally simply related to the initial preferred orientation; often, however, the relationship is not simple, but complicated and obscure in origin.¹ The orientations of crystals formed by precipitation from solid solutions have been shown by many studies in this and other countries to be determined by the orientation of the crystals of the solid solution stable at the higher temperatures, though here again complicated cases have been found and no general theory is available.² Related to this latter class are the relationships found in crystals formed by suppressed transforma-

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¹ E. Schmid and G. Wassermann: *Handbuch der phys. u. tech. Mechanik* (1931) **4**, 2d half, 319-351. Barth, Leipzig.

² R. F. Mehl and coworkers: Studies upon the Widmanstätten Structure, I-VI. *Trans. A.I.M.E.* (1931 to 1933); *A.I.M.E. Tech. Pubs.* 521 and 539 (1934).

O. T. Marzke: Precipitation of Alpha from Beta Brass. *A.I.M.E. Contribution* 29(1933).

J. Weerts: Transformation Process in Beta Brass and in Beta Silver-zinc Alloys. *Ztsch. f. Metallkunde* (1932) **24**, 265-70.

M. Straumanis and J. Weerts: Liberation of the Alpha Phase in Beta Brass. *Ztsch. Physik* (1932) **78**, 1-16.

D. W. Smith: A Study of Segregate Structures in Copper-tin and Silver-zinc Alloys. *Trans. A.I.M.E.* (1933) **104**, 48-68.

M. L. Fuller and J. L. Rodda: Segregate Structures of the Widmanstätten Type Developed from Solid Solutions of Copper in Zinc. *Trans. A.I.M.E.* (1933) **104**, 116-130.

In principle, studies on orientation relationships in suppressed constitutional changes are in no way different from the work cited here; see references of footnote 3.

tions in the solid state, notably in crystals of the tetragonal and cubic structures in martensite, but also in others;³ transformations in pure metals have been shown to exhibit similar orientation relationships.⁴

Indeed, the wide-spread occurrence of such orientation relationships suggests strongly that most if not all crystals formed in crystalline matrices inherit their orientations from the matrix crystals.⁵

The orientations obtaining in eutectoid structures formed normally at the eutectoid temperatures, however, have not been studied successfully. Work has been reported on structures obtained by quenching alloys of eutectoid composition, notably β Cu-Al alloys, and orientation relationships have been discovered,⁶ but in no case was the structural arrangement of the constituents as seen under the microscope the lamellar structure typical of the eutectoid structure as formed at or just below the eutectoid temperature. Inasmuch as the formation of the constituents in rapidly cooled alloys is known to be quite different from that in slowly cooled alloys where the reaction takes place at or near to the eutectoid temperature, differing both in the sequence of appearance and even in the composition and structure of the phases formed,⁷ and more nearly resembling simple precipitation from solid solutions than transformation at a eutectoid temperature, we may conclude that these studies afford no direct information on the crystallographic mechanism of a true eutectoid inversion.

The possibility of orientation relationships in the eutectoid pearlite in iron-carbon alloys has been discussed from the beginning of metallog-

³ G. Kurdjumow and G. Sachs: Über den Mechanismus der Stahlhärtung. *Ztsch. Phys.* (1930) **64**, 325. See reviews by L. Graf [Transformations in the System Gold-copper. *Ztsch. Metallkunde* (1932) **24**, 241-247] and by G. Sachs [General Laws of Structure and Property Changes Accompanying Transformation Processes. *Ztsch. Metallkunde* (1932) **24**, 248-255].

G. Wassermann: Transformation Processes in Beta Aluminum-bronze. *Metallwirtschaft* (1934) **13**, 133-139.

I. Isaitschew and G. Kurdjumow: Transformations in Copper-tin Eutectoid Alloys, I. *Phys. Ztsch. Sowjetunion* (1934) **5**, 6-21.

W. Bugakow, I. Isaitschew and G. Kurdjumow: Transformations in Copper-tin Eutectoid Alloys, II. *Phys. Ztsch. Sowjetunion* (1934) **5**, 22-30.

⁴ R. F. Mehl and D. W. Smith: Studies upon the Widmanstätten Structure, V.—The Gamma-alpha Transformation in Pure Iron. *A.I.M.E. Tech. Pub.* 521 (1934).

Partial results on Co and Ti have been reported by U. Dehlinger: Mechanism of Allotropic Transformation in Cobalt and Thallium. *Metallwirtschaft* (1932) **11**, 223-235; and also by U. Dehlinger, E. Osswald, and H. Bumm: Transformation in Single Crystals of Cobalt. *Ztsch. Metallkunde* (1933) **25**, 62-63.

⁵ R. F. Mehl: Discussion. *Trans. A.I.M.E.* (1933) **105**, 257-258.

⁶ G. Wassermann and G. Kurdjumow: References of footnote 3.

⁷ C. S. Smith and W. E. Lindlie: A Micrographic Study of the Decomposition of the Beta Phase in the Copper-aluminum System. *Trans. A.I.M.E.* (1933) **104**, 69-115.

raphy. Sorby⁸ thought it "extremely probable that the direction of the alternating plates was determined by the previous crystalline structure." This idea was developed later by Belaiew in a series of papers;⁹ Belaiew assumed that the lamellae of ferrite and cementite in pearlite are parallel—not to crystallographic planes in the original austenite (and in this way differed from Sorby and other writers) but to planes in the ferrite itself. He relates that a count of the number of directions taken by the lamellae on a surface of polish within a single austenite cell is not more than 12 and probably is 12,¹⁰ and concludes from this that the lamellae are parallel to the {210} planes in ferrite.¹¹

The group of pearlite crystals originating in the decomposition of a single crystal of austenite is sometimes called an "austenite cell"; within this cell it is familiarly observed that the pearlite is divided into more or less distinct areas, which are designated as "pearlite grains," in which the lamellae have approximately a common position in space. It is an old observation that the ferrite within a pearlite grain possesses but one orientation: there is no evidence of grain boundaries at points where the ferrite from several lamellae becomes continuous, and the orientation of etch pits in the ferrite is a common one throughout the pearlite grain.¹² The orientations of the ferrite in different pearlite grains within the same austenite cell, however, are different. There is some evidence that the cementite lamellae within a pearlite grain also have a common orientation, for the cleavage edges of cementite lamellae formed by polishing are apparently identical in position; this evidence, however, is based upon rather indistinct structures observed at very high magnifications.¹³

Evidently a count of the number of directions taken by the lamellae within an austenite cell can furnish little evidence for a parallelism between the lamellae and any plane in the ferrite, for the several orientations of ferrite within an austenite cell mentioned in the preceding paragraph and demonstrated in the present work would multiply the usual number of planes of given indices; a 12-family plane, therefore, would be represented by n times 12 planes where n is the number of different orientations of ferrite within a given austenite cell.

Despite many studies there is no real evidence at present for a definite number of lamellae directions within an austenite cell. When pearlite

⁸ H. C. Sorby: On the Application of Very High Powers to the Study of the Microscopical Structure of Steel. *Jnl. Iron and Steel Inst.* (1886) **28**, 140–144.

⁹ A bibliography of Belaiew's many papers may be found in his book, *La Cristallisation des Metaux*. 3d Conference, Inst. de Soudure Autogene, Paris, 1934.

¹⁰ N. T. Belaiew: Discussion. *Jnl. Iron and Steel Inst.* (1932) **125**, 330.

¹¹ The selection of the {210} plane cannot be justified, since there are many other planes in the cubic lattice with 12 to the family.

¹² W. Rosenhain: Discussion. *Jnl. Iron and Steel Inst.* (1922) **105**, 201–227; also reply by N. T. Belaiew

¹³ N. T. Belaiew: Reference of footnote 12.

is formed at a slow cooling rate the lamellae are straighter (in three dimensions, flatter) than when formed at a fast cooling rate. At fast cooling rates, when pearlite forms at temperatures considerably lower than A_1 , the lamellae become wavy and tend to assume radiating structures, forming rosettes, in which the directions of the lamellae vary greatly from point to point.¹⁴ This is true also of eutectoids in other systems.¹⁵ But pearlite formed even at slow cooling rates under the best conditions shows too great a deviation in direction, both for a single lamella and for a group of lamellae within a single pearlite grain, to enable an observer to associate them with any crystallographic plane.

It is, of course, quite possible that the original nucleus of pearlite may exhibit lamellae accurately aligned with some crystallographic plane in the austenite, and from the data to be presented in this paper such a possibility seems real. However, the conditions affecting the subsequent growth of the lamellae appear to be more important in determining the spatial distribution of the two constituents than purely crystallographic relationships.

It is known that orientation relationships may exist between matrix and precipitate phase when the outward form of the precipitate crystal gives no hint of such a relationship.¹⁶ Such a relationship, therefore, may exist in pearlite even though the directions of the pearlite lamellae do not suggest it. Attempts by Iwensen and Kurdjumow to determine such a relationship by a direct X-ray analysis of the orientations of ferrite present in troostite or fine-grained pearlite were unsuccessful and led Kurdjumow at first to argue against such a relationship; recently, however, he has stated the belief that such a relationship exists but that the ferrite orientations may be so greatly distorted by volume changes accompanying the eutectoid inversion that no analysis is possible.¹⁷

ORIENTATION OF FERRITE IN PEARLITE

It is the purpose of the present work to demonstrate a relationship in orientation between ferrite in pearlite and the austenite from which it formed.

¹⁴ There are several early references to this fact. See recent work by H. C. H. Carpenter and J. M. Robertson: The Austenite \rightleftharpoons Pearlite Inversion. *Jnl. Iron and Steel Inst.* (1932) **125**, 309-328.

¹⁵ C. S. Smith and W. E. Lindlief: Reference of footnote 7.

¹⁶ See discussion on this point, especially in relation to grain-boundary segregate: R. F. Mehl and O. T. Marzke: Studies upon the Widmanstätten Structure, II.—The Beta Copper-zinc and the Beta Copper-aluminum Alloys. *Trans. A.I.M.E.* (1931) **93**, 123-161; also R. F. Mehl, C. S. Barrett and D. W. Smith: Studies upon the Widmanstätten Structure, IV.—The Iron-carbon Alloys. *Trans. A.I.M.E.* (1933) **105**, 215.

¹⁷ A. Iwensen and G. Kurdjumow: *Jnl. d. phys. Chem.* (Russian) **1**, 41 (1930).

G. Kurdjumow: Über den Mechanismus der Phasenumwandlungen in den Eutectoidlegierungen. *Phys. Ztsch. der Sowjetunion* (1933) **4**, 488-500.

The phases that participate in the formation of pearlite are austenite, ferrite, and cementite; ferrite is body-centered cubic in lattice structure, austenite face-centered cubic, and cementite complex orthorhombic.¹⁸ These crystal structures are also those that participate in the formation of the Widmanstätten figures in slowly cooled hypoeutectoid and hypereutectoid iron-carbon alloys. The orientation relationships in slowly cooled hypoeutectoid alloys, in which austenite and proeutectoid ferrite are the participating phases, have been completely analyzed and found identical to those obtaining in martensite. The orientation relationships in slowly cooled hypereutectoid alloys, in which austenite and proeutectoid cementite are the participating phases, have been only partially analyzed, owing to difficulties inherent in the structure.¹⁹ Since the same lattices participate in the formation of pearlite, we might well expect to find relationships similar to one or the other of these two cases. It is not known, however, which of the two phases, ferrite and cementite, form first from austenite (assuming that they do not form simultaneously), nor do we know whether both take their orientation from the austenite or whether one alone does so, forming first, and the other takes its orientation from the first. Thus we cannot predict the orientations taken by either of the two phases.

EXPERIMENTAL TECHNIQUE AND RESULTS

It was not found possible to determine a crystallographic plane in the austenite to which the pearlite lamellae lay parallel, for pearlite lamellae in the sample studied were not flat but wavy (see below) to such a degree that crystallographic analysis of their positions, as by the use of trace direction frequency curves, led to no useful result. This is in conformity with the experience of others, as stated above. The work is therefore limited to a determination of the orientations of the phases involved without reference to any plane of precipitation.

The first attempt at analysis was performed upon a grain of pearlite of eutectoid composition, approximately 1.5 cm. in diameter, separated from a matrix of other grains which had been held for a very long time at a high temperature, thus growing an unusually large austenite grain.

¹⁸ The best X-ray data on these phases are given in the following articles:

Alpha iron—M. C. Neuburger: Lattice Constants, 1933. *Ztsch. Krist.* (1933) **86A**, 395-422.

Fe₃C—A. Westgren: The Crystal Structure of Cementite. *Avtryck Ur Jernkontorets Ann.* (1932) 457-468.

Austenite—H. Esser and G. Müller: Lattice Constants of Pure Iron and Iron-carbon Alloys at Temperatures up to 1100°. *Archiv f. d. Eisenhüttenwesen* (1933) **7**, 265-268.

¹⁹ R. F. Mehl, C. S. Barrett and D. W. Smith: Reference of footnote 16.

Thin wedge sections were cut from this and subjected to the standard X-ray face-pole figure analysis. It was hoped that the symmetry of the resultant pole figure would lead to the placing of the important symmetry axes in the parent austenite, a task that could not be accomplished in any other way.

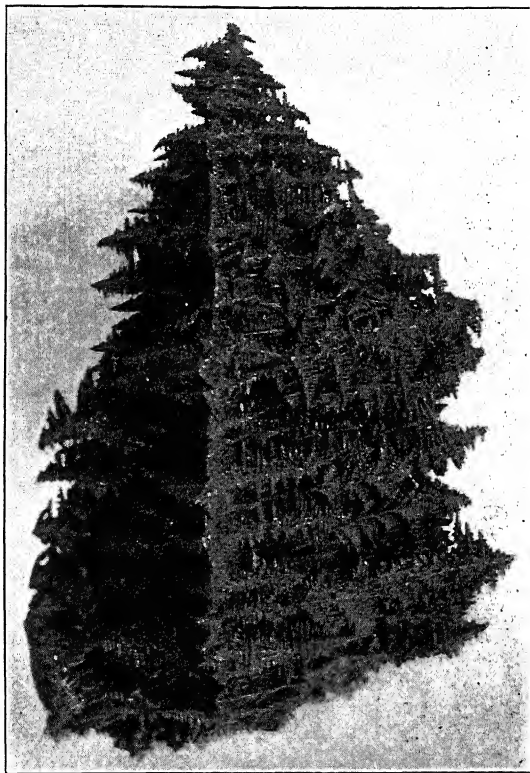


FIG. 1.—DENDRITE OF EUTECTOID STEEL. $\times 2.5$.

X-ray photographs taken from this sample showed intensity maxima on the white radiation $\{110\}$ circle, which retained their azimuthal positions upon moving the piece in a direction perpendicular to the X-ray beam. This is proof that the ferrite possesses a small number of regular orientations rather than a large number of random orientations. The completed pole figure, however, showed no symmetry and work on this sample was abandoned. Apparently the volume change at the eutectoid inversion had altered the orientations of the ferrite crystals to such a degree that no general symmetry in their distribution could be discovered.

A much more useful sample was then chosen for analysis. This was an unusually well formed dendrite, shown in Fig. 1, obtained from the

pipe of an ingot of eutectoid steel of the following composition: 0.75 per cent C, 0.022 P, 0.75 Mn, 0.24 Si, 0.023 S.²⁰ The axes of the dendrite were three in number, made evident by the long spurs shown in Fig. 1. Throughout the dendrite these spurs varied in angular position appreciably, but within small regions the spurs were accurately arranged at right angles to one another. Evidently, then, these place the cube axes of the original austenite crystal which formed directly from the melt.²¹ The dendrite displayed a very open network structure in which only small regions were solid. This condition doubtless prevented a wide-spread and cumulative distortion during the volume change accompanying the eutectoid inversion. The microscopic structure of the sample (Fig. 2) showed it to be wholly pearlitic with no trace of either proeutectoid ferrite or cementite.²²

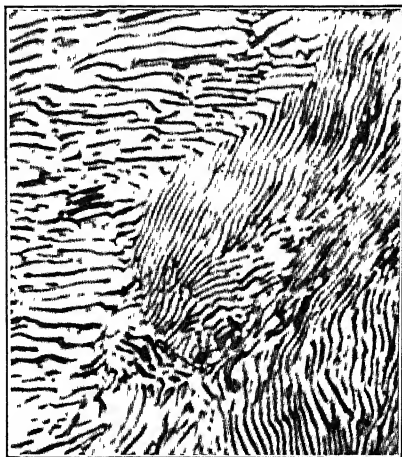


FIG. 2.—MICROSTRUCTURE OF DENDRITE OF EUTECTOID STEEL. ETCHED WITH ONE PER CENT NITAL. $\times 1500$.

A small region of this dendrite was selected and from it a small disk-shaped sample was cut with one surface accurately perpendicular to one of the spur directions. This surface thus lay parallel to one of the cube faces of the original austenite. As cut, the specimen was approximately 0.05 in. thick; by careful polishing and etching, this thickness was reduced to 0.015 in. Between the next to the final operation of polishing and etching and the final operation the sample was sealed in an evacuated glass tube, annealed for $\frac{1}{2}$ hr. at 450° , and cooled with the furnace for the purpose of relieving stresses without causing recrystallization.

The sample was then mounted in an X-ray camera with the spur direction normal to the disk made parallel to the X-ray beam (the disk face normal to the X-ray beam) and another spur direction made parallel to the axis about which the sample was subsequently to be rotated.

²⁰ We owe this dendrite to the kindness of Mr. W. J. Reagan, of the Edgewater Steel Co., Oakmont, Pa. Mr. Reagan states that this steel was killed with silicon in the furnace and titanium additions were made in the ladle; apparently the addition of titanium favors the development of dendrites in the pipe.

²¹ This observation is consistent with previous observations. See N. T. Belaiew, reference of footnote 9, and G. Kurdjumow and G. Sachs, reference of footnote 3.

²² From the known effect of manganese and silicon upon the carbon content corresponding to a eutectoid composition, it may be shown that the composition given above corresponds very closely to eutectoid composition.

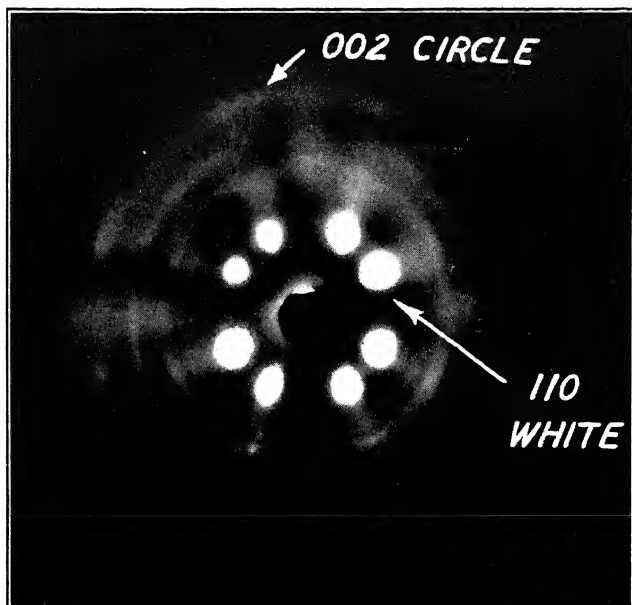


FIG. 3.—X-RAY PHOTOGRAPH OF DISK FROM DENDRITE, TAKEN AT 0° TO DISK NORMAL.
REPRODUCED FROM CONTACT PRINT.

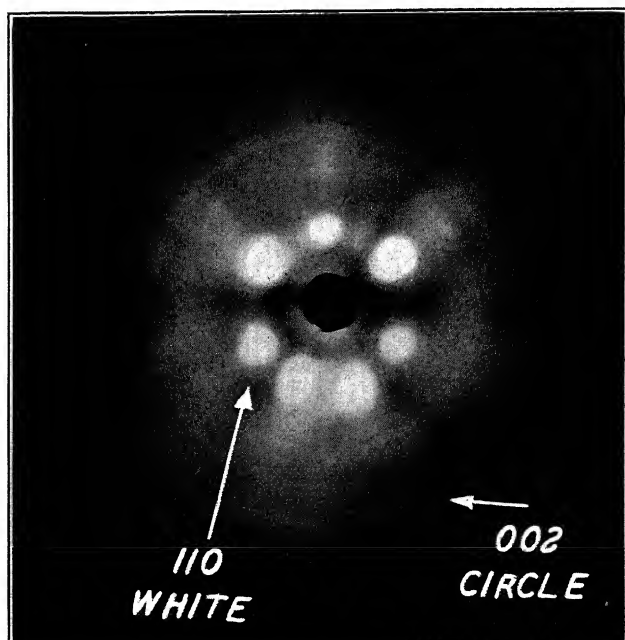


FIG. 4.—X-RAY PHOTOGRAPH OF DISK FROM DENDRITE, TAKEN AT 40° TO DISK NORMAL.
REPRODUCED FROM CONTACT PRINT.

Starting with this position nine photograms were taken in 5° intervals on either side of the initial position, making 19 in all. Unfiltered radiation from a molybdenum target was used; the specimen-to-film distance was 5 cm., and the exposure times varied from 180 milliampere-hours at an angle of inclination of 0° to 555 ma-hr. at an angle of inclination of 45° . Two of the photograms obtained, respectively 0° and 40° from the initial position, are reproduced in Figs. 3 and 4. The maxima on the white radiation $\{110\}$ circle are clear in the figures; those on $\{002\}$ circle from the molybdenum $K\alpha$ line are less distinct, but amply distinct for measurement on the original photogram.

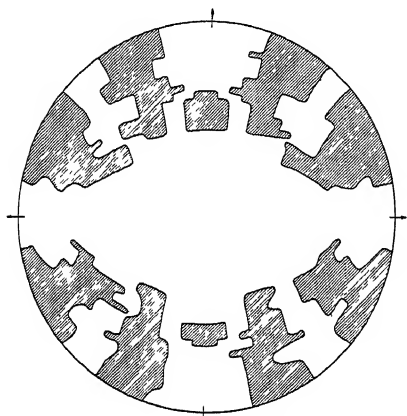


FIG. 5.

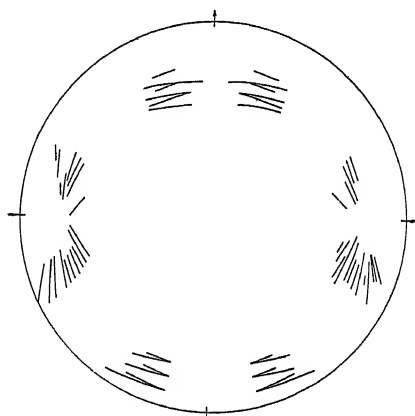


FIG. 6.

FIG. 5.— $\{110\}$ POLE FIGURE FROM WHITE RADIATION MAXIMA. ARROWS SHOW CUBE DIRECTIONS IN AUSTENITE.

FIG. 6.— $\{100\}$ POLE FIGURE DERIVED FROM $\{002\}$ CIRCLE. ARROWS SHOW CUBE DIRECTIONS IN AUSTENITE.

The azimuthal angular positions and the peripheral spread of the intensity maxima on both circles were measured and plotted stereographically, with the surface of the sample, corresponding to a $\{100\}$ austenite plane, as the plane of projection. The pole figure obtained from plotting the white radiation intensity maxima, which gives a $\{110\}$ pole figure, is shown in Fig. 5; that obtained from the $\{002\}$ circle, which gives a $\{100\}$ pole figure, is shown in Fig. 6. Owing to the wider band of radiation used, extended areas are shown in Fig. 5, whereas Fig. 6 obtained by the use of the molybdenum $K\alpha$ line shows only a series of lines defining the pole areas. The pole areas from Figs. 5 and 6 may be rotated into one quadrant in order to multiply in effect the number of crystals. This procedure, augmented by cubic symmetry operations, gives more complete pole figures, shown in Figs. 7 and 8.²³

²³ Compare with R. F. Mehl and D. W. Smith: reference of footnote 4.

DISCUSSION OF RESULTS

The pole figures given in Figs. 7 and 8 thus represent merely the orientations of the ferrite in relation to the orientation of the original austenite, and give a mechanism by which these ferrite orientations originate only by inference. The orientations of the ferrite crystals with respect to the austenite may be expressed in terms of crystal planes and directions in the following way. It is assumed that a certain type of plane in the ferrite lies parallel to a certain type of plane in the austenite, and further that certain directions in these planes also lie parallel; on the basis of this assumption a projection of the predicted orientations of the ferrite crystals is prepared (Figs. 7 and 8). The set of parallel planes and directions in the two lattices, among the many possible, that gives projection poles most nearly corresponding with the observed pole figure areas may be used in describing the orientations observed. The lack of exact correspondence between the predicted poles and the observed pole figure areas is to be ascribed to disturbing effects, chiefly lattice distortion. If it is further assumed that the plane in the ferrite actually formed from the plane in austenite to which it lies parallel, we have a possible mechanism for the formation of the ferrite. It must be clearly borne in mind, however, that such a correspondence between pole figure areas and predicted pole positions is in general no proof that the postulated mechanism actually operated during the transformation. In simple cases, such as that of the transformation of gamma into alpha iron, it may be so taken with great certainty, but in complicated cases such as the present, there must be considerable uncertainty, as will be pointed out. Despite these limitations the method of analysis is a fruitful one.

Such an analysis may be performed in the present case, assuming for the moment that the ferrite orientations originate *directly* from the austenite lattice. As stated above, it is a reasonable supposition that these ferrite orientations should originate from austenite by the mechanism experimentally demonstrated for proeutectoid ferrite in hypoeutectoid steels and for the ferrite in martensite; namely, the mechanism described crystallographically as follows:

$$\begin{aligned} \{111\}_{\gamma} &\parallel \{110\}_{\alpha} \\ [110]_{\gamma} &\parallel [111]_{\alpha} \end{aligned}$$

in which the stated directions lie in the selected planes. The pole figure demanded by such a mechanism is shown in Figs. 7 and 8 by open circles. It is evident that this cannot be the mechanism since some of these circles fall in regions of the projection not covered by pole areas. This is more clearly shown in Fig. 8 than in Fig. 7.

In a survey of other possible mechanisms a search was made for planes and directions in the two lattices, austenite and ferrite, which showed

similarity in atomic patterns and interatomic distances, for previous work has indicated the fundamental importance of such similarities in determining precipitation or transition mechanisms. Six such orientation relationships were inspected,²⁴ as follows: (1) $\{111\}\gamma \parallel \{110\}\alpha$, $[110]\gamma \parallel [111]\alpha$; (2) $\{100\}\gamma \parallel \{100\}\alpha$, $[100]\gamma \parallel [110]\alpha$; (3) $\{211\}\gamma \parallel \{210\}\alpha$, $[110]\gamma \parallel [100]\alpha$; (4) $\{311\}\gamma \parallel \{211\}\alpha$, $[112]\gamma \parallel [110]\alpha$; (5) $\{321\}\gamma \parallel \{331\}\alpha$, $[331]\gamma \parallel [321]\alpha$; (6) $\{110\}\gamma \parallel \{112\}\alpha$, $[112]\gamma \parallel [110]\alpha$. This list could have been continued indefinitely, but any additional combinations would have included planes and directions of such low atomic population as to lose plausibility.

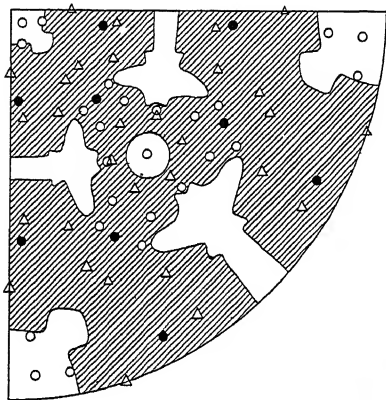


FIG. 7.

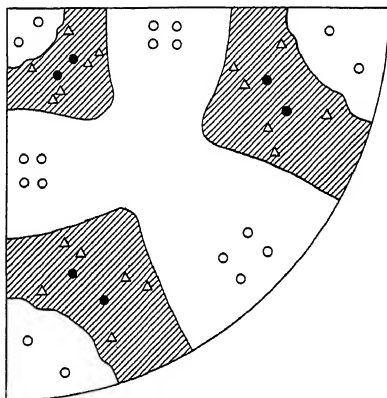


FIG. 8.

FIG. 7.—ONE QUADRANT OF POLE FIGURE SHOWN IN FIG. 5. OPEN CIRCLES SHOW IDEAL MECHANISM No. 1; TRIANGLES, No. 5; FILLED CIRCLES, No. 6.

FIG. 8.—ONE QUADRANT OF POLE FIGURE SHOWN IN FIG. 6. POLES GIVEN BY IDEAL MECHANISM SHOWN AS IN FIG. 7.

Only two of these orientation relationships satisfy the experimentally determined pole figure; namely, numbers 5 and 6. Both solutions are shown in Figs. 7 and 8, No. 5 by small triangles and No. 6 by filled circles. No. 6 seems the more likely of the two, for the planes and directions assumed are simpler and more densely packed with atoms, though No. 5 seems to explain the observed pole areas more completely. No real choice between the two ideal orientation relationships can be made.²⁵

²⁴ No attempt has been made in writing this list of indices to select a particular plane of the family of planes of the form $\{h k l\}$ and particular directions which lie in the particular planes. Both plane and direction indices are left in a general form, but the requirement that the directions indicated must lie in the planes selected is to be understood.

²⁵ Either of these mechanisms may be analyzed into two sets of shearing movements. (See R. F. Mehl and D. W. Smith: Reference of footnote 4.) In view of the uncertainty in the choice of the proper orientation relationships, it does not seem useful to perform such analysis. For the same reasons no comparison of atom patterns and interatomic distances is made.

Evidently, then, the mechanism of formation of ferrite in pearlite from austenite is not that for proeutectoid ferrite in hypoeutectoid steels or in martensite. It must not be inferred, however, that the above constitutes a proof of the selected mechanism: It merely states that if ferrite inherits its orientation directly from austenite, the mechanism selected will explain the observed ferrite orientations. If, however, the cementite in pearlite takes its orientation from the austenite, and the ferrite in turn takes its orientation from the cementite, the selected mechanism is purely fictitious, summing up two mechanisms in a meaningless combination.

The fact of the existence of a small number of determinate orientations of ferrite, however, cannot be doubted from Figs. 7 and 8, despite the random nature of the directions of the lamellae in the sample, as shown in Fig. 2. The orientation of ferrite in pearlite is determined, directly or indirectly, by the orientation of the parent austenite.

SUMMARY

The orientations of ferrite in pearlite with respect to the original austenite have been determined by X-ray methods and expressed upon a conventional pole-figure diagram. It was found that ferrite in pearlite assumes a discrete number of determinate orientations rather than an infinite number of random orientations. These orientations bear a direct relationship to the orientation of the original austenite and are proof that the orientation of ferrite in pearlite is determined directly or indirectly by the orientation of the austenite. Two ideal orientation relationships between ferrite and austenite are given, both of which will account for the observed ferrite orientations. The more probable relationship is one in which a $\{112\}$ plane in the ferrite lies parallel to a $\{110\}$ plane in the austenite, and a $[110]$ direction in this $\{112\}$ plane in the ferrite lies parallel to a $[112]$ direction in this $\{110\}$ plane in the austenite. The orientation relationships observed are quite different from those between proeutectoid ferrite and austenite in slowly cooled hypoeutectoid steels and between ferrite and austenite in martensite, and suggest that the mechanism of formation of ferrite in pearlite is different from that in the latter two cases.

Reactions in the Solid State, I—Initial Course of Subcritical Isothermal Diffusion Reactions in Austenite in an Alloy Steel

BY HOWARD A. SMITH,* MEMBER A.I.M.E.

(New York Meeting, February, 1935)

OF late considerable experimental and theoretical interest has been shown in the rates of transformation from a single phase, usually a supercooled solid solution, into one or more phases. Such reactions may involve both diffusion and transformation of the major constituent, as in iron alloys, or it may simply involve diffusion, as in superstructure formation and in age-hardening systems.

Most of the work has been confined to ferrous alloys^{1-9†} although two investigations have been made on copper alloys^{10,11}. That such work may be of considerable practical importance has been demonstrated by Bain¹², by the workers at the Kaiser Wilhelm Institut für Eisenforschung^{13,14}, and by the everyday use of precipitation and age-hardening principles¹⁵. Experiments in this country have generally followed Davenport and Bain's technique of rapid supercooling followed by isothermal treatment. In Germany^{16,17} the work has been extended to the study of the influence of accurately controlled and measured rates of cooling.

The work on steel indicates that there are two subcritical temperature ranges where reaction starts sooner after quenching and proceeds at a more rapid rate than at other temperatures. At subcritical temperatures above A_r'' (temperature of martensite formation) where reaction is dependent upon atomic migration there is a period of time of which the length depends upon the alloy content and the temperature, before which no reaction has been detected. Davenport and Bain¹ find that different sorts of atoms in solid solution in gamma iron affect the length of this "prereaction" period differently, manganese probably being the most effective in lengthening it. It is very difficult to believe that nothing occurs within these "prereaction" regions, for if this were so there is no reason why any reaction at all should be observed. In the light of experimental facts and theoretical considerations it is certainly

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† References are at the end of the paper.

tenable that some reaction proceeds within this seemingly dormant period. The hypotheses of Bragg and Williams¹⁸, and of Upton¹⁹, the formation of superstructures²⁰ and the definite crystallographic relations²¹ existing between austenite and the products of its decomposition, indicate that the solute atoms undergo a transition from a random to a final stable ordered arrangement. Hengstenberg and Wassermann²² have even obtained experimental evidence of intermediate atomic configurations, other than superstructure formation, in a 4 per cent Cu-Al alloy.

A review of the work on the rates of reactions in metallic systems shows that there has been a variety of methods used for measuring these rates and that at most only two methods have been used in ferrous systems by any one investigator on any one alloy. It is thus difficult to make a true comparison of the relative merits of the different methods or to say when any one method may be used to the best advantage.

Thus there were two motives for the present investigation: (1) to make a particular study of the initial stages of the isothermal reaction of a selected alloy, carrying the measurements at least to a point where the rate of reaction of the major portion of the alloy is at the maximum; (2) to follow through the initial stages and major portion of the isothermal reaction of the same alloy using as many different methods as practicable and to make a comparative study of the value of each method.

ALLOY, HEAT TREATMENT AND EXPERIMENTAL METHODS

The alloy selected for this work was a hypereutectoid manganese steel of the following composition: 6.48 per cent Mn, 0.92 C, 0.013 S, 0.19 Si and 0.037 P, the remainder being iron. This is alloy No. 19 as used by Bain, Davenport and Waring²³. Fig. 1 is the constitutional diagram for iron and carbon at the 6.5 per cent Mn section, according to these authors, and only represents the condition of the austenite prior to any atomic diffusion. A vertical line is drawn across the diagram at a composition corresponding to that of steel No. 19. There are several distinct advantages in using this alloy. It is not only material of which the general behavior has been well investigated by Bain and his coworkers, but one about which we already have information concerning reaction characteristics². There is a sufficient "prereaction" period and a slow enough reaction to permit a detailed study of the isothermal reaction from the instant of quenching to the complete reaction at a reasonable working temperature. Also, in this alloy the Ar'' point is below room temperature, so that the austenite will be retained as such upon quenching without martensite formation. Even ordinary cooling rates are quite sufficient to allow the passage of the Ar' (temperature of minimum prereaction period) point safely without formation of eutectoid.

The steel as received was in the as-forged condition and had a 1.3-cm. square cross-section. This material was homogenized (to eliminate

manganese segregation) by heating in quartz in an atmosphere of argon for 12 hr. at 1200° C. The charge came up to temperature in 4 hr. and was furnace-cooled to room temperature in 9 hr. All samples for use in the experiments to be mentioned later were made of this homogenized material. The grain diameter in this state varied from 25 to 150 μ . Every sample before reaction was homogenized (to reduce carbon segregation) by heating in vacuo in a tube furnace for 30 min. at tem-

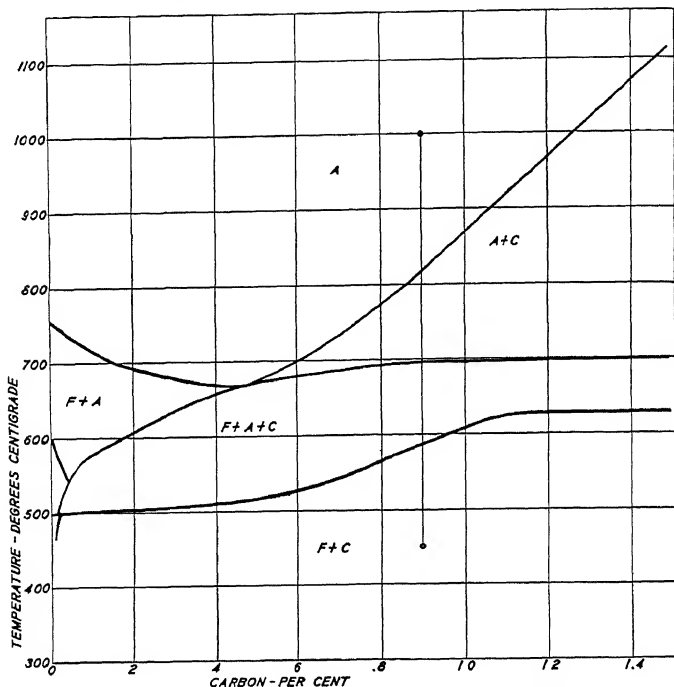


FIG. 1.—6.5 PER CENT MANGANESE SECTION OF THE Fe-Mn-C SYSTEM.

peratures between 1010° and 1020° C. as measured by a thermocouple driven into a slot in the sample. The alloy came up to temperature in 55 min. and was at a temperature above A_1 (695° C.) for about an hour and above the A_{cm} (820° C.) for 45 min. before quenching. The sample was supported by the thermocouple, which in turn was supported by an iron rod. This rod, as well as the thermocouple, was led out through a quick-release stopper, which served for a convenient handle for transferring the sample to the lead bath at 450° C. $\pm 2^\circ$ C.,* and from there into a large quantity of water for the room-temperature quench. With such an arrangement, the sample could be transferred from the furnace at 1010° C. to the lead bath at 450° C. in about a second and from the

* It was found necessary to give the lead bath a positive direction of flow with a mechanical stirrer to obtain this close control. Otherwise convection currents caused momentary fluctuations of as much as 10° to 15° C.

lead bath to the water at 10° to 15° C. in about the same time. Samples representing zero holding time at 450° C. were quenched from the furnace directly into the water.

The temperature and time of homogenization and the isothermal reaction temperature were selected after a number of dilatometer runs correlated with microscopic examination. The data taken from these dilatometer experiments are plotted in Fig. 2 as the time necessary for the

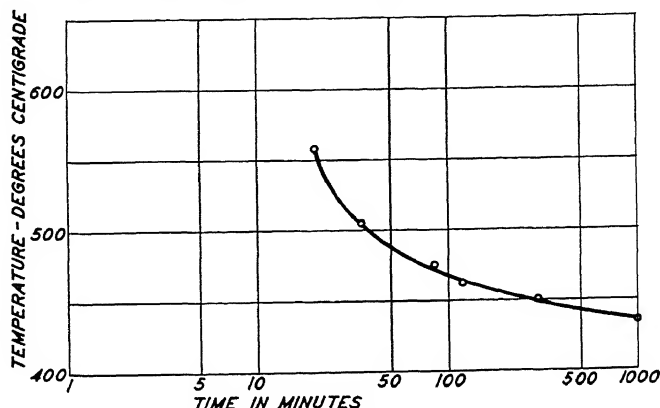


FIG. 2.—TIME OF MAXIMUM DENSITY FOR VARIOUS ISOTHERMAL TEMPERATURES.

sample to attain its maximum density at different constant temperatures (see Fig. 10). Such a curve closely parallels one corresponding to the beginning of the eutectoid reaction. From the course of this curve, and from the observation that 558° C. is close to the temperature of minimum reaction period^{1,6} in other steels, it would seem that the Ar' point for this steel lies between 550° and 575° C.

The methods employed for following the course of the reaction in the alloy, after having received the heat treatment described, included microscopic observation and measurements of dilation, electrical conductivity, magnetic permeability, hardness, lattice parameter (a_0) and monochromatic X-ray diffraction line width. Of these only the dilatometric, electrical conductivity and magnetic measurements were made at 450° C., the others being made at room temperature on quenched samples. The microscopic, dilatometric, electrical conductivity and magnetic methods have been employed principally for estimating amounts of transformation where the major part, if not all, of the original solid solution transforms. Hardness, a_0 , and line widening have more generally been used for the usual age-hardening systems where only a small part of a new phase ever appears from the original solid solution.

MICROSCOPIC AND DILATOMETRIC MEASUREMENTS

The microscopic samples, 13 mm. square and 3 to 4 mm. thick, were heat-treated according to the procedure outlined above. These samples were held at 450° C. according to the schedule in Table 1.

TABLE 1.—*Partial Reaction Times for the X-ray, Microscopic and Hardness Samples*

| MINUTES | MINUTES | MINUTES | MINUTES | MINUTES | MINUTES |
|---------|---------|---------|---------|---------|---------|
| 0 | 30 | 70 | 150 | 400 | 2,015 |
| 3 | 40 | 80 | 200 | 615 | 3,505 |
| 10 | 50 | 100 | 250 | 800 | 3,920 |
| 20 | 60 | 120 | 300 | 1,000 | 17,200 |

After receiving the treatment shown in Table 1, the samples were used for X-ray, microscopic and hardness examination. After removing $\frac{1}{2}$ mm. from the surface by grinding, each was finished with No. 1 alumina followed by either No. 3 alumina or MgO. A sodium picrate etch was given to all samples, but samples held for longer than 300 min. were given an additional light etch in 4 per cent nital. The latter treatment for the samples containing rather large amounts of eutectoid served better to delineate the remaining austenitic areas. The course of the reaction in the initial stages may be followed in the photomicrographs in Figs. 3 to 7; Fig. 8 is a characteristic structure after 1000 minutes.

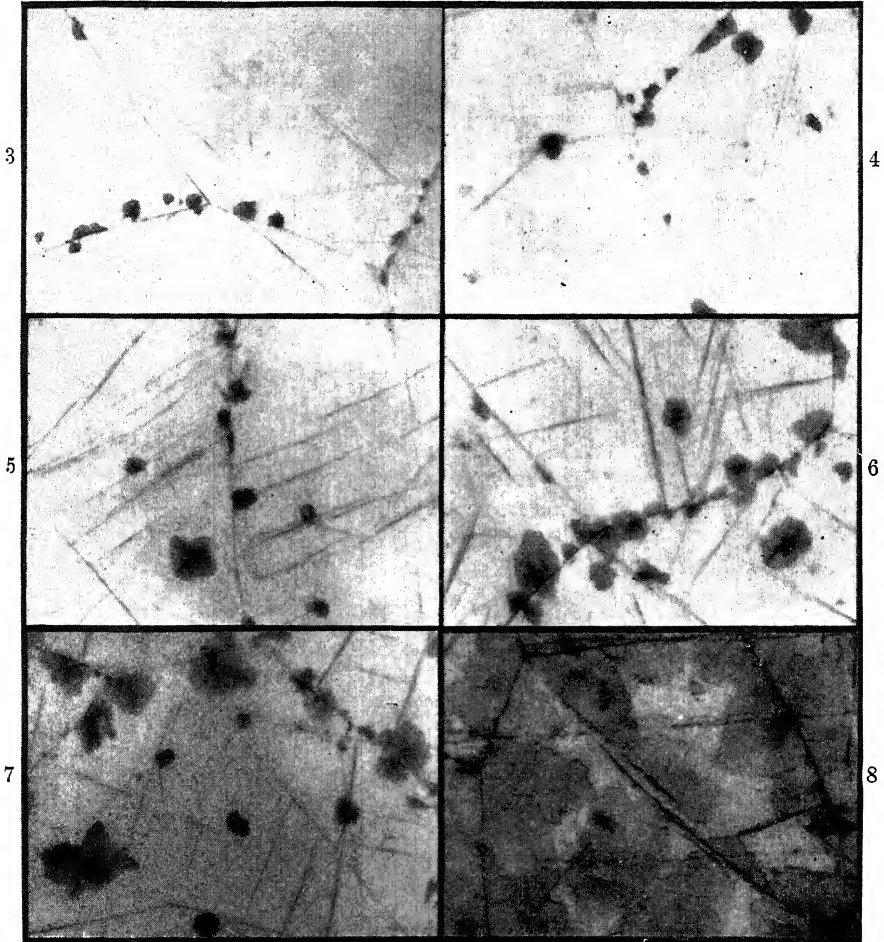
Numerical values for expressing the course of the reaction were obtained by cutting out the eutectoid and the austenite plus carbide areas and weighing each. In Fig. 9 the reaction curves obtained from these measurements are given. Since the carbide separates out in thin sections along the grain boundaries and as Widmanstätten plates within the austenite crystals, the carbide curve was estimated from Figs. 3 to 7, from the variation of the lattice parameter with time (Fig. 16), and from the calculated volume percentage of the amount of the proeutectoid carbide that would separate out. The maximum amount of carbide precipitation, 6 per cent, can be considered as approximate only because of the influence of the degree of supercooling on the separation of proeutectoid constituents^{1,2,19}, which in this alloy is unknown. A value of 0.52 per cent carbon was selected arbitrarily as the upper limit of the eutectoid composition for this calculation. In Table 2 is given the initial course of the reactions as detected at a magnification of 2800.

TABLE 2.—*Initial Course of Reactions*

| HOLDING TIME, MIN. | FIRST TRACES |
|--------------------|-------------------------|
| 30 | Intergranular carbide |
| 50 | Intergranular eutectoid |
| 60 | Intragranular carbide |
| 70 | Intragranular eutectoid |

The dilatometer used was nearly identical in the details of construction with that of Davenport and Bain¹. All essential parts of the instrument were made of kovar²⁴, a Westinghouse austenitic alloy of low known coefficient of expansion. Before a series of readings was made, the

dilatometer was allowed to stand in the lead bath at 450°C. for at least an hour, so that it would reach thermal equilibrium. The sample was either inserted directly into the dilatometer, which was momentarily



FIGS. 3-8.—TRANSFORMATION PRODUCTS.

- Fig. 3.—After 75 minutes at 450°C. $\times 2000$.
 Fig. 4.—After 150 minutes at 450°C. $\times 2000$.
 Fig. 5.—After 200 minutes at 450°C. $\times 2000$.
 Fig. 6.—After 250 minutes at 450°C. $\times 2000$.
 Fig. 7.—After 300 minutes at 450°C. $\times 2000$.
 Fig. 8.—After 1000 minutes at 450°C. $\times 2800$.
 All reduced one-third; original magnification given.

raised from the bath, from the homogenizing furnace at 1010°C. and quenched in position in the instrument or was first quenched in the lead and then inserted into the dilatometer. The latter method gave the more rapid quench but the sample may not have seated so well. As the results were the same in either case, the first procedure usually was used. The

samples were 7.2 cm. long, 1.2 cm. wide, and from 2 to 3 mm. thick. Care was taken to remove all material deficient in manganese and carbon by grinding 0.3 mm. from all outside surfaces before heat treatment, so that the resulting curve would be truly representative of the steel. The course of the isothermal reaction (change in length with time) at 450° C. is shown in Fig. 10.

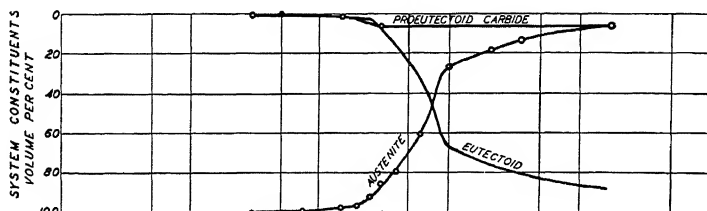


FIG. 9.—MICROSCOPIC REACTION CURVE.

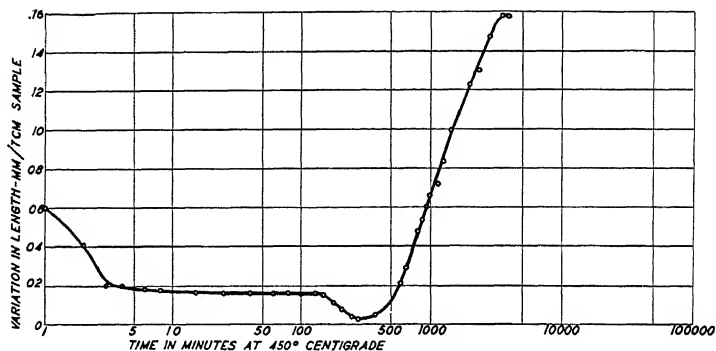


FIG. 10.—DILATOMETER REACTION CURVE.

ELECTRICAL CONDUCTIVITY AND MAGNETIC PERMEABILITY MEASUREMENTS

The sample used for the conductivity measurements was made of a 15-cm. length of stock and was slotted with a cutting wheel as shown in Fig. 11. This final sample was approximately four times as long and had a cross-section of less than one-fourth of the original bar. Thoroughly annealed current leads of No. 4 nichrome wire were welded to the protruding ends at the right of the sample. Potential leads of No. 18 nichrome wire were silver-soldered to the current leads 1 cm. from the welded junction between the current leads and the sample.* A thermocouple was wedged into the small slot in the upper left end of the

* Similar results were obtained when the potential leads were made of steel similar to the sample and welded to it with an oxyacetylene flame.

sample (Fig. 11). The current, potential and thermocouple leads were brought out through the quick-release stopper. The sample thus mounted was homogenized as usual, quenched in the lead bath, held for one minute and immediately transferred to a tube furnace at 450°C ., which was then evacuated. The first conductivity reading was made 2 min. after the sample was removed from the lead bath. The sample was so placed that the temperature difference between the ends amounted to about 0.5°C . The temperature of the conductivity furnace varied from 447° to 454°C . Readings of potential drop, current and temperature were made as close together as possible, usually within 10 sec. Temperature corrections were applied to the conductivity readings from experimentally determined temperature coefficients of resistivity for the alloy. For the alloy from $t = 0$ to $t = 250$ min. (austenite) this coefficient amounted to 0.0013 at 450°C ., and for the alloy from $t = 7630$ to $t = 7690$ min. (eutectoid) the coefficient was 0.0053 at 450°C . After holding at 450°C . for 9500 min., the sample was allowed to cool in the furnace to room temperature, conductivity readings being made simultaneously. Only the usual increase of conductivity with falling temperature was noted. Fig. 12 shows the course of the reaction according to these measurements.

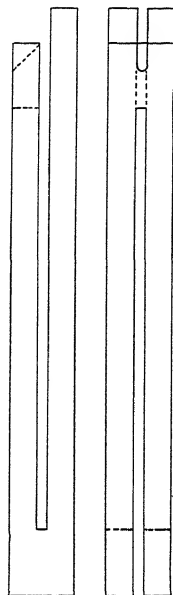


FIG. 11.—ELECTRICAL CONDUCTIVITY SPECIMEN.

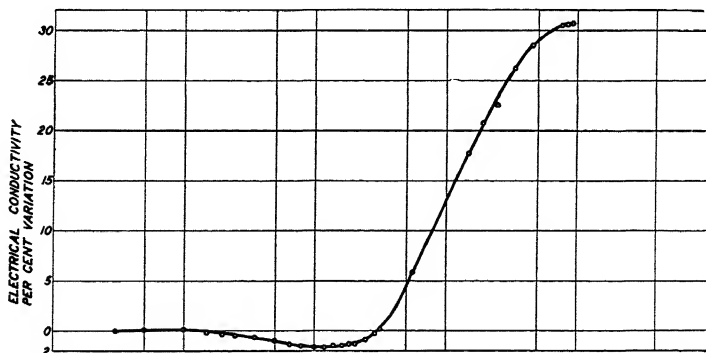


FIG. 12.—ELECTRICAL CONDUCTIVITY REACTION CURVE.

conductivity sample. The construction and operation of the special reaction furnace used is described by Walters and Eckel²⁵. The temperature of the furnace, however, was held constant in the work described

here, there being a temperature difference of 1.3°C. between the ends of the sample. An impressed magnetizing force of 100 gilberts per centimeter was maintained. The coil ratios were so adjusted that no galvanometer throw was observed, either when the furnace was charged with

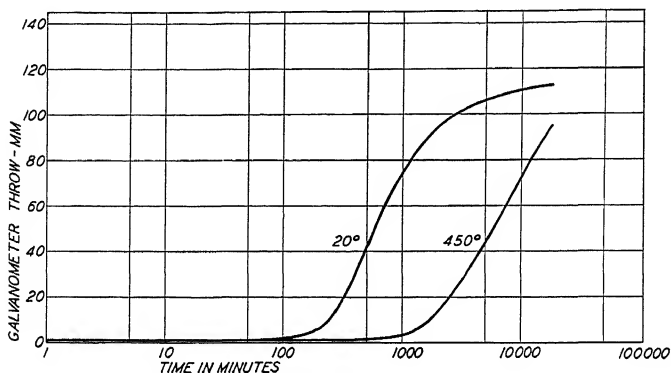


FIG. 13.—MAGNETIC FLUX REACTION CURVE.

a nonmagnetic material or when it was empty. The maximum throw for the sample treated for 17,200 min. and then furnace-cooled was just over 11 cm. The reaction curve is shown in Fig. 13, showing the relation between the magnetism as measured at 450° and 20°C. Fig. 14 shows the reaction occurring with the cooling down of the sample in

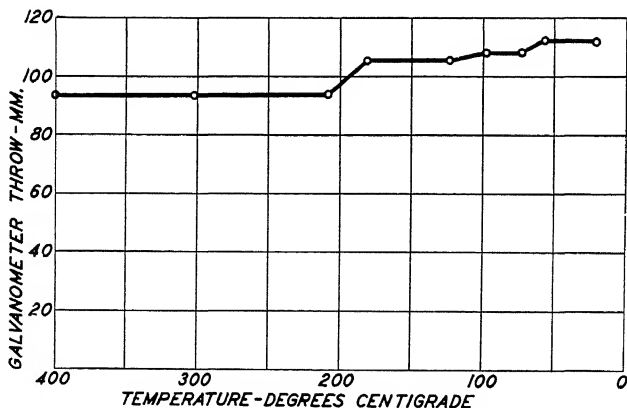


FIG. 14.—VARIATION OF MAGNETIC FLUX WITH FALLING TEMPERATURE AFTER 17,500 MIN. AT 450°C.

the furnace after reaction. The inflection points in the curve between 210° and 180°C. are caused by passing through the Curie point of cementite. The inflection points between 120° and 100°C. and between 70° and 60°C. are probably related to the formation of martensite from the residual austenite, which is impoverished somewhat in carbon and manganese. The composition of this residual austenite,

of course, is questionable, so that the temperature of these breaks cannot be associated as martensite points with any definite composition of austenite.

HARDNESS MEASUREMENTS

The samples used for the hardness measurements were those used for X-ray and subsequently for microscopic examination, and were described above. The time-hardness curve for samples quenched from 450° C. is shown in Fig. 15. Each point represents the average of 10 measurements on one sample. The hardness was read on the Rockwell C scale, using a Brale point with a 150-kg. load.

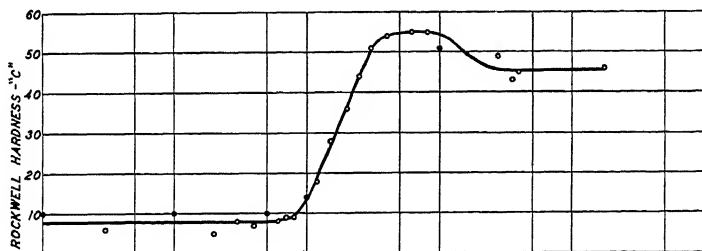


FIG. 15.—HARDNESS REACTION CURVE.

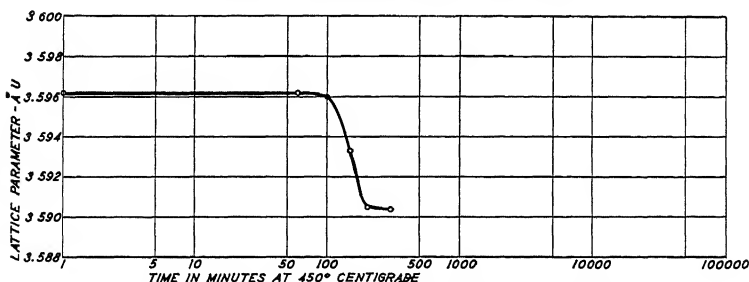


FIG. 16.—LATTICE PARAMETER (a_0) REACTION CURVE.

a_0 , and Line Width Measurements

After the sample had been heat-treated for X-ray examination, from 0.50 to 0.75 mm. was ground from the surface, the samples being then plane polished on Nos. 1, 0, 00 and 000 emery paper. They were then carefully etched in a mixture of 75 per cent concentrated nitric acid and 25 per cent water, by volume, to remove all traces of martensite formed by the cold work of grinding and polishing. This etching had to be done in a considerable number of short-time etches, in order to avoid heating the sample.

All X-ray photographs were made on Barrett's²⁶ design of a Sachs' back-reflection camera, and with the exception of one set of exposures all were made with both the film and the sample rotating. A divergent beam from a large focal spot was used, the Bragg focusing conditions

being observed for the (113) plane of austenite and CrK_β radiation. All of the film to sample distances employed were close to 6.6 cm. In all cases a single film of five exposures was made with the same filament at 20 kv. and 25 ma. in about 3 hr. Eastman safety tinted base film, 12.7 by 17.8 cm., was used. As the coefficient of thermal expansion of austenite is considerable, record of the temperature variations throughout an

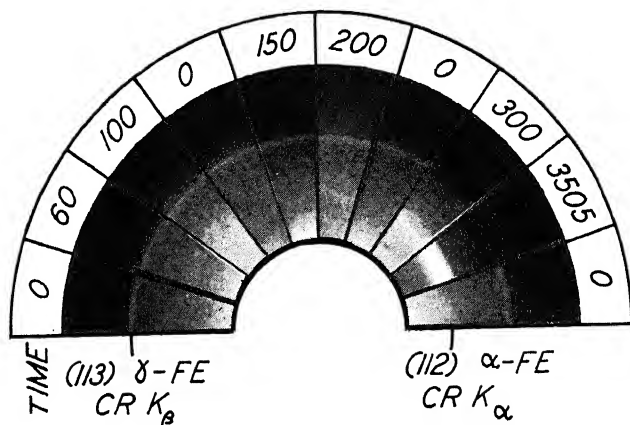


FIG. 17.—THE CrK_β (113) LINE OF GAMMA IRON AND THE CrK_α (112) LINE OF ALPHA IRON AFTER VARIOUS TIMES AT 450°C . FILM AND SAMPLE ROTATED.

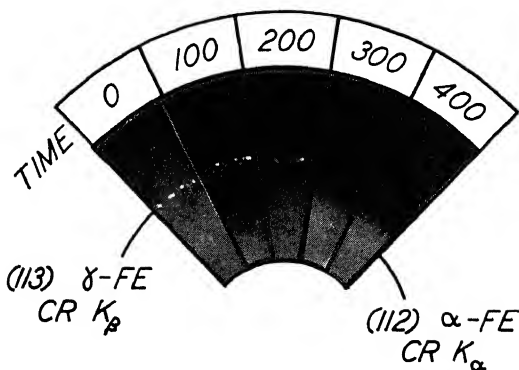


FIG. 18.—THE CrK_β (113) DIFFRACTION SPOTS OF GAMMA IRON AFTER VARIOUS TIMES AT 450°C . FILM AND SAMPLE STATIONARY.

exposure was made and corrections applied to the a_0 measurements in two instances where necessary.

The individual points in the a_0 -time curve in Fig. 16 represent the average of eight readings, four on each of two sets of lines, made on a comparator reading directly to thousandths of a millimeter. Fig. 17 is a composite positive showing the (113) K_β line of austenite after various times of isothermal treatment. Fig. 18 is a similar positive where neither the sample nor the film was rotated.

Microphotometric curves from the same lines used for parameter measurements show that up to $t = 100$ min. no definite change in line width occurred. For $t > 100$ min., however, there is a progressive increase in the width of the lines up to $t = 300$ min. beyond which it was impossible to see the austenite line even though this phase was present to the extent of about 85 per cent by volume (see Fig. 9). The increasing width and haziness of the individual crystal diffraction spots due to deformation caused by eutectoid formation and to increasing scatter of the individual diffraction spots due to increasing differences in the parameter of different crystals²⁷. Fig. 18 indicates that both of these factors are

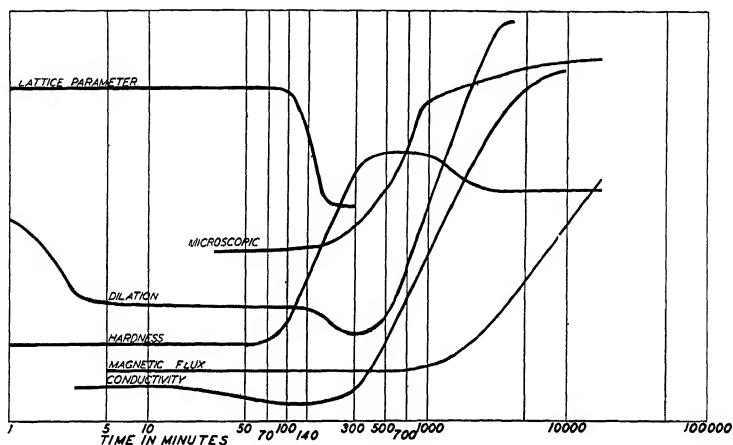


FIG. 19.—GRAPHIC SUMMARY OF THE REACTION CURVES.

effective. The cause of the disappearance of the line at about $t = 300$ is probably due more largely to the crystal distortion than to the scatter of individual diffraction spots. It may be noted that the diffraction spots are sharper at 100 min. than at any other time. This did not make itself evident in the photometer curves of the lines in Fig. 17.

DISCUSSION OF RESULTS

Relationships between the Reaction Curves

In Fig. 19 all of the curves for the various methods of following the reaction are correlated on the basis of the same time scale. It is at once apparent that no two methods are directly measuring the same quantity. This wide divergence in reaction characteristics indicates that each method has its own peculiarities and perhaps its own usefulness. It would seem worth while, therefore, to examine the details of these methods, using the microscopic one as a basis for comparison. This

method for estimating the volume percentage^{1,10} of the reaction products for a given history is perhaps the standard both because very small traces of new phases may be detected and because where there is more than one phase formed from the original solid solution each phase usually may be distinctly separated from the others present. Also microscopic and etching technique is backed by a greater wealth of experience and more confidence therefore is placed on the results of such a method. The method is limited by the resolution obtainable at high magnifications²⁸ and its accuracy is determined by the methods used for estimating the relative amounts of the constituents present. As illustrated by the present investigation, this method may fail to give any indication of significant variations in the composition of the various phases; here, in the composition of the austenite.

The dilatometer has been used for following the course of isothermal reactions in systems where the major portion of the original solid solution transforms and also in aging systems^{1,7,29}. This instrument under proper conditions indicates minute changes in the density of the system, and where the system is not too complicated it is capable of making very fine distinctions. Where more than one phase separates from solid solution, and particularly where the composition of the forming as well as of the decomposing phases may vary, as in these manganese steels, care must be used in interpreting the results. The reason is thus evident for the difference between the dilatometer reaction curve and the microscopic one. For a period of time from $t = 50$ to $t = 140$ min., the proeutectoid carbide precipitation proceeds simultaneously with the eutectoid reaction. The density of the proeutectoid and eutectoid carbide as well as of alpha iron is less than that of the austenite. These two reaction products form at such rates that the decrease in density of the sample nearly balances the increase in density due to a characteristic rate of separation of carbon from solid solution in gamma iron, and the resultant density of the sample is approximately constant. Then from $t = 140$ to $t = 300$ there is an increase in density because the proeutectoid carbide forms a small volume percentage of the total sample and because its rate of formation is much more rapid than that of the formation of the eutectoid. The inflection point at $t = 300$ represents a point of maximum density not so much because this time is significant in either reaction but because the carbide reaction is decelerating rapidly and the eutectoid reaction is accelerating rapidly, so that the latter reaction overtakes the former and the density begins to decrease. Thus the dilatometer curve in Fig. 19 gets a later start than the microscopic curve and lags behind through the larger part of its course. It may be concluded, then, that while the dilatometer gives an accurate account of over-all density it does not give a true picture of the relative amounts of various constituents at any given time for this alloy.

Electrical conductivity measurements have been used frequently for studying equilibrium diagrams but less frequently for aging^{11,30} or for investigations of reaction involving larger amounts of phase transformation^{8,10}. The form of the conductivity curve in Fig. 12 is similar to those of Wever and Jellinghaus⁸ for a 0.89 per cent C, 0.61 per cent Mn steel held for reaction at temperatures from 260° to 330° C. The significant difference in their curves lies in the lack of the initial decrease of conductivity. It is believed that if these authors had worked with a slowly reacting steel, as was done in the present investigation, this initial decrease would have been found. Wever and Jellinghaus find that the observed conductivity reaction curves may be as much as 13 per cent below son Frey's³¹ theoretical value at 50 per cent transformation. Whatever the explanation of the course of these conductivity curves may be, they fail to be useful in giving directly an accurate idea of the amount of the precipitated phases present at any given time in this alloy. We shall return to this point later.

Magnetic measurements of various kinds have often been used for phase-rule studies²⁵ and for the development of alloys for special purposes. In a few instances magnetic permeability measurements have been utilized for following the course of isothermal reactions in ferrous systems^{5,6}. The remarkable difference in magnetism at 450° and 20° C. (see Fig. 13) offers an explanation for the sluggishness of the magnetic reaction. These curves show that 450° C. is above the Curie temperature for any of the phases present at 700 min. but that this temperature is below the Curie point for one, at least, of the phases present at 15,000 min. This behavior may logically be explained by the formation, up to 700 min., of eutectoid structures whose components are a carbide low in manganese and a gamma iron structure low in carbon but high in manganese. For times greater than 1000 min. this austenite begins to lose appreciable amounts of manganese by diffusion into the carbides, in which state the system has lower energy, and the transformation temperature of increasingly larger amounts of the eutectoid austenite is raised above 450° C. It thus appears that in interpreting magnetic curves for any but a binary system due consideration must be given to the temperature and time of reaction as well as to the difference in the rates of diffusion of the different kinds of atoms present. We should, therefore, view with some skepticism the interpretation that Wever and Lange^{5,6} place on their work.

While there seems to be no definite all-inclusive scientific concept of hardness for metallurgical products, such measurements have been used extensively for following age-hardening in alloys. Davenport and Bain¹ have measured the hardness of various steels after complete reaction at various temperatures, and Smith and Lindlief¹⁰ have followed the reaction in a nonferrous system by measuring the hardness of samples

quenched after various reaction times at various temperatures. Since hardness is affected by so many factors³², each alloy and its history must be studied as an individual case. It may be said, however, that hardness as determined by impressions is, in general, a measure of the availability of slip planes for slip and of the ease with which slip can occur on a given family of such planes.

As Fig. 19 and Table 2 show, the hardness begins a definite increase at about the time the intragranular carbide appears microscopically and has reached 90 per cent of its maximum value at 300 min. where the dilatometer reaction is just starting and the proeutectoid carbide has probably all appeared together with 10 per cent of the eutectoid product. There is nothing at all in the hardness reaction curve to indicate the course of the proeutectoid carbide reaction as distinct from the eutectoid reaction. From Fig. 15 it may be seen that maximum hardness occurs at $t = 700$ min., at which time about 50 per cent of the eutectoid reaction has taken place. As might be expected, this time of maximum hardness corresponds closely to that necessary for the formation of a continuous network of intergranular eutectoid. Photomicrographs at $t = 615$ show a continuous network of intergranular eutectoid while the eutectoid at 400 min. has not yet become large enough to be contiguous. The rapid and early rise of hardness may be explained by the precipitation of the proeutectoid carbide and as the eutectoid reaction proceeds simultaneously (Table 2) if more slowly, the property of hardness is insensitive to which type of product causes its rise. After about $t = 700$ min. the hardness begins to decrease, probably owing to the increase of particle size by coalescence in the eutectoid. The hardness increase in the proeutectoid carbide reaction is due mainly to the decrease in the availability of slip planes in the austenite by precipitation of a new phase, while in the eutectoid reaction the additional effects of small grain size and crystal structure come into the problem.

If minute effects are considered, any variation of lattice parameter (position of monochromatic diffraction line) probably involves, at least momentarily, unevenness in atomic reflecting planes (width of monochromatic diffraction line) sometime during the process of change. The inverse of this may also be true. In either case the effects may occur in small and relatively few atomic regions, so that the net results on the diffraction line would not be found. The factors that influence a_0 are foreign atoms in solid solution in the solvent lattice and microscopic strain. The latter factor is usually very much the smaller of the two while the type of solid solution and of the foreign solute atom and its structural configuration in the solvent lattice determines the magnitude of the variation in a_0 . The factors that may influence the line width are microscopic lattice disorders due to strain produced externally and to

strain produced both by any type of solid solution, and microscopic and macroscopic inhomogeneities of composition²².

The use of a_0 determinations together with well controlled methods of thermal treatment have been used extensively for obtaining solubility limits in equilibrium diagrams³³, and in a few cases in recent years such measurements have been used to determine the course of separation of the solute atoms from the solvent lattice³⁰. The a_0 proeutectoid carbide reaction curve in Fig. 19 follows closely the dilatometric carbide curve. The dilatometer reaction is somewhat slower because these measurements represent simultaneously the formation of some eutectoid. The a_0 -carbide curve lags somewhat (50 min.) behind the first microscopic intergranular carbide but much less so (20 min.) for the intragranular carbide. This failure to conform to or even to precede the microscopic proeutectoid carbide curve is no doubt due to the really very small percentage of the matrix affected by the first traces of precipitation, particularly of the intergranular sort. A comparison of Figs. 3 to 7 with Fig. 15 shows that the major portion of parameter change corresponds nicely with the time of maximum proeutectoid carbide precipitation. Line-width measurements have been used to measure microscopic lattice distortion caused by elastic deformation and by solid solution aging^{22,34} and may be used as a measure of macroscopic solid solution inhomogeneities³⁵. In measurements made on this alloy, the line widening occurring for $t = 100$ min. is ascribed to the latter effect.

Initial Stages in Decomposition of Austenite

The initial stages in the decomposition of this alloy may be outlined as follows:

1. The electrical conductivity decreases from $t = 10$ to $t = 110$ min., the most rapid decrease occurring between $t = 20$ and $t = 100$.
2. The density increases from $t = 140$ to $t = 300$, the most rapid increase occurring between $t = 150$ and $t = 250$.
3. The hardness increases from $t = 60$ to $t = 600$, the most rapid increase taking place between $t = 80$ and $t = 300$.
4. The lattice parameter decreases from $t = 80$ to $t = 300$, the most notable decrease being between $t = 100$ and $t = 200$.
5. Monochromatic diffraction line widening is not appreciable until $t = 120$ minutes.
6. Intergranular carbide first appears at $t = 30$; intergranular eutectoid first appears at $t = 50$; intragranular carbide first appears at $t = 60$, intragranular eutectoid first appears at $t = 70$.
7. Magnetic permeability data give practically no indication of any change in the alloy until $t = 700$.

Conductivity measurements give the first indication of some change taking place in the supersaturated solid solution, and with the possible

exception of hardness and microstructure the total decrease in conductivity occurs before any other measured change of sensible magnitude. This decrease represents a 1.7 per cent change as compared to a 1.4 per cent change in a 4.3 per cent Cu-Al alloy³⁰ aged at room temperature. The first increase in hardness corresponds closely to the first indication of intragranular carbide, which is as it should be, but even at $t = 100$, at which time the decrease in conductivity is largely complete, there is very little volume percentage of other constituents than austenite. In attempting to explain the course of the conductivity curve, the question arises as to the influence of various factors on the conductivity. In general, it may be said³⁶ that the electrical conductivity of a solid solution decreases with additional amounts of a solute atom and decreases with increase in microscopic strain. Generally, the conductivity of an intermetallic compound is greater than that of the solid solutions on either side of it in composition. The conductivity of a mixture of physically distinct homogeneous phases varies according to the theoretical predictions of G. von Frey³¹ with regard to the amount, the type of distribution, and the relative conductivities of the various phases present. We know that the conductivity of the austenite must be low because of the amount of the carbon in solid solution. The relative conductivity of the ferrite is doubtful, and it would seem that the conductivity of the carbide is greater than that of the original austenite.*

If this is the state of affairs, we have, to start with, a matrix of low conductivity wherein appear minute disconnected masses of other phases of higher conductivity. This is von Frey's case III, and although the conductivity is relatively insensitive to even large masses of better conducting constituents we would still predict an increase of conductivity. In addition to these considerations, the gamma iron solid solution is being impoverished continually of carbon by precipitation, which should also cause an increase in conductivity. If quenching strains exist there should be an initial increase in conductivity from the relief of such strains. In spite of the tendency of all of these factors to cause an increase of conductivity, we still get an initial decrease, which must be explained on other grounds.

Wever and Jellinghaus⁸ working with a 0.35 per cent C, 0.80 per cent Cr and 4.04 per cent Ni steel found from simultaneous measurements that there was a definite difference between the amount of transformation indicated by the conductivity curves and by the magnetic curves. This difference was interpreted to indicate that as conductivity is sensitive to conditions of the solid solution and permeability is supposedly sensitive

* While we are dealing here with amounts of carbon in solid solution of about half that necessary for complete saturation, in analogy with other systems the conductivity of the austenite should still be much lower than that of the compound.

to actual phase separation, changes were taking place in the austenite before the actual appearance of the eutectoid.

That some configurations of the carbon atoms other than statistical may form previous to appearance of a new phase has been suggested by Öhman³⁷ and has been used by Wever and Lange⁶ in explaining the various reactions occurring in steels. Upton¹⁹ also assumes that some pre-precipitation reactions take place. In any case there must exist some sort of transitory configurations of the solute atoms other than statistical

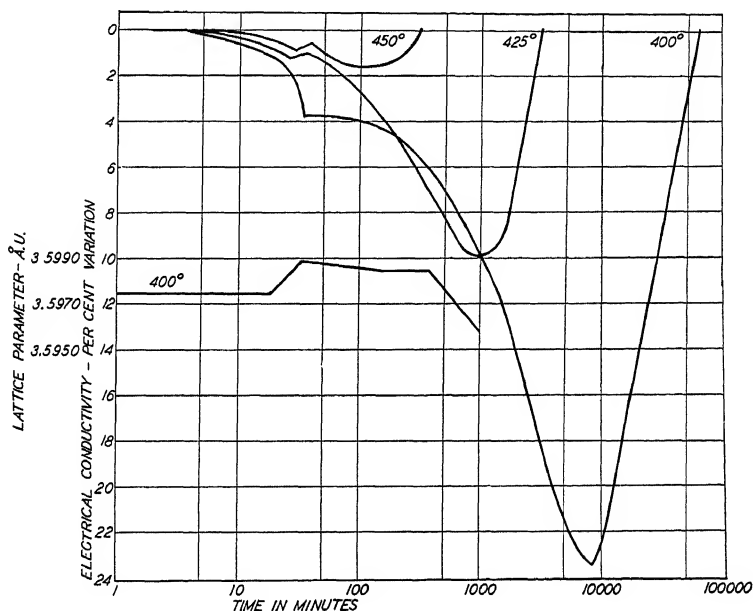


FIG. 20.

previous to the formation of new phases by diffusion processes. But it seems doubtful whether the fact of the failure of the conductivity reaction curve to coincide with the magnetic curve can be cited for such evidence.* It is believed that Wever and Lange failed to find this initial decrease in conductivity because they worked with a steel that reacted more than 100 times faster than the one considered here.

Fig. 20 correlates the initial portions of the conductivity reaction curves taken at 450°, 425° and 400° C. and the lattice parameter curve for the reaction at 400° C. At about 35 min. there is an abrupt change in lattice parameter and in the conductivity curves. All of these changes

* From permeability measurements on samples quenched after various reaction times it has been found that 450° C. is above the Curie point for the very fine ferrite particles in the eutectoid areas. The Curie point may vary with time, then, at 450° C., owing to the migration of Mn atoms from the ferrite to the carbide.

occur strictly within the one-phase solid solution. This sudden change in the unit cell is probably tetragonal or orthorhombic distortion (as indicated by the splitting of the (222) K_α line). The maximum lineal increase in size amounts to about 0.5 per cent. As the diffraction lines are sharpened simultaneously the resulting atomic configuration may be a superstructure involving carbon and iron atoms. Since this change in structure, whatever it may be, is associated with a definite amount of energy as evidenced by the discrete changes occurring, it is a pseudostable state in the diffusion process.

It seems better to offer the initial decrease in conductivity as positive evidence of certain pre-precipitation atomic arrangements that are intermediate between the initial statistical distribution of solute carbon atoms and the final metallic compound which has certain definitely fixed positions for the carbon atoms in a definite lattice structure. Similar suggestions have been made³⁸ for explaining the behavior of the conductivity of Al-Cu age-hardening alloys and by H. Meyer³⁹ to explain age-hardening in the Al-Zn system. Numerous other systems where aging depends on changes occurring in a supercooled solid solution show this behavior. The decomposition of austenite exhibits peculiarities of its own. Like Cu-Al alloys aged at room temperature, there is very little if any change in lattice parameter and line widening^{22,30}, but unlike these there is no definite dilatometric²⁹ evidence of reaction. Unlike most aging systems no definite increase of hardness was found previous to the actual microscopic appearance of a new phase.

One other peculiarity in the decomposition of this solid solution at constant subcritical temperatures should be mentioned. There is an easily visible overlapping of the proeutectoid and eutectoid reactions, each proceeding at different rates, which, no doubt, are functionally related. While the equilibrium relationships for this alloy are definitely fixed^{23,40}, only a little is known² about the details of its behavior as affected by various rates of cooling and by various subcritical constant-temperature treatments. For instance, it is not known for alloy steels generally just what spread in eutectoid composition occurs at various constant subcritical temperatures preceded by rapid quenching. In consequence no definite prediction can be made regarding the relative times of appearance of the proeutectoid and the eutectoid reactions. It seems logical that there should be considerable overlapping of these reactions as contrasted with a very slow cooling treatment where substantial equilibrium exists at each temperature and the two reactions are quite distinct.

SUMMARY

The initial stages in the decomposition of austenite in an alloy steel have been investigated at a constant subcritical temperature of 450° C.

This steel, Bain, Davenport and Waring's alloy No. 19, with 6.48 per cent Mn and 0.92 per cent C, is a slowly reacting one, which allows a detailed observation of the reaction processes. Microscopic observations and measurements of dilation, electrical conductivity, magnetic permeability, hardness, lattice parameter and monochromatic X-ray diffraction-line width have been made throughout the course of the reaction. Microscopic observations are considered most reliable for determining the volume percentage of the various phases present. Direct estimation of the volume percentage of the phases present from other reaction curves may be in considerable error. Magnetic methods have shown the possibility of diffusion of manganese atoms in gamma iron in the presence of carbides at 450° C. Marked changes in conductivity and lattice parameter taking place within the austenite just before appearance of the proeutectoid carbide indicate that there is at least one definite preliminary stage in the rearrangement of the atoms in the austenite before the appearance of the carbide. Each type of measurement has its own usefulness, and all of these, with some additional methods, are considered necessary for the difficult study of the rearrangements proceeding within the solid solution previous to and during the formation of new phases.

ACKNOWLEDGMENTS

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Some Effects of Copper in Malleable Iron*

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(New York Meeting, February, 1935)

A STUDY of the precipitation-hardening of copper steels¹ led the authors to investigate malleable iron containing copper, for the low-carbon ferritic matrix in malleable iron should lend itself admirably to precipitation-hardening. It was soon found that in addition to rendering malleable iron susceptible to improvement by precipitation-hardening treatments, copper has another potentially useful effect as an accelerator of graphitization. Brief mention of these effects was given in a general paper by Lorig and one of the present authors²; the present paper gives further details on the graphitization and precipitation-hardening effects only. After the completion of this work a paper by L. Lykkin³ appeared, confirming the authors' conclusions regarding graphitization.

MATERIAL USED

After some preliminary heats had been made in the laboratory to determine the effect of copper, several castings from commercial air-furnace heats were obtained, and data from these alone are given here. Part of the metal was poured directly and part was treated in the ladle with the desired amount of copper before pouring. Green-sand molds were used, each holding two tensile test pieces of the form adopted by the Malleable Iron Research Institute, or two bars for graphitization studies, $\frac{5}{8}$ in. in diameter and 9 in. long, fed through two enlarged sections equidistant from the middle and ends of the bars. Risers of suitable size insured sound castings. Tensile tests were made on the castings after commercial malleableizing and after special heat treatments to be described. The analyses of the white irons are given in Table 1.

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¹ C. S. Smith and E. W. Palmer: *Trans. A.I.M.E.* (1933) **105**, 133.

² C. H. Lorig and C. S. Smith: *Trans. Amer. Foundrymen's Assn.* (1934).

³ L. Lykkin: *Jnl. Sci. Iowa State College* (1933) **8**, 207.

TABLE 1.—*Analyses and Graphitization Studies on Commercial Heats of White Iron, with and without Ladle Additions of Copper*

| Group | Alloy No. | Composition, Per Cent | | | | | | Spec. No | First-stage Graphitization ^a | | Second Stage at 725° C. Time, Hr. |
|-------|-----------|-----------------------|------|------|-------|-------|------|----------|---|-----------|-----------------------------------|
| | | C | Si | Mn | P | S | Cu | | Temperature, Deg. C. | Time, Hr. | |
| 3/27 | 1651 | 2 40 | 1 01 | 0 31 | 0.144 | 0.075 | 0 0 | D | 925 | 6 8 | 13.2 14 8 21 8 |
| | | | | | | | | F | 925 | 7.5 | |
| | | | | | | | | I | 925 | 8 0 | |
| | | | | | | | | J | 890 | 14 7 | |
| | | | | | | | | K | 850 | 37 5 | |
| 3/27 | 1652 | 2 40 | 1.01 | 0 31 | 0.144 | 0 075 | 1.33 | D | 925 | 4 2 | 6 0 11.2 19.7 |
| | | | | | | | | F | 925 | 5 2 | |
| | | | | | | | | G | 890 | 8 7 | |
| | | | | | | | | H | 850 | 24 5 | |
| 3/27 | 1653 | 2 40 | 1.01 | 0 31 | 0 144 | 0.075 | 1.73 | A | 925 | 4 0 | (5 5) |
| 3/27 | 1655 | 2 40 | 1 01 | 0 31 | 0.144 | 0.075 | 2 94 | A | 925 | 2.4 | 4.5 |
| 5/19 | 1731 | 2 64 | 0 91 | 0 26 | 0 159 | 0.070 | 0.05 | A | 925 | 12 1 | 18 3 |
| 5/19 | 1732 | 2 64 | 0 91 | 0 26 | 0 159 | 0.070 | 1 22 | A | 925 | 5.7 | 8 2 |
| | | | | | | | | B | 925 | 5 7 | |
| 7/7 | 1761 | 2 61 | 1 00 | 0.29 | 0.143 | 0 075 | 0 01 | A | 925 | 9 8 | 11 8 |
| 7/7 | 1762 | 2 61 | 1 00 | 0.29 | 0 143 | 0 075 | 1 03 | A | 925 | 5 7 | 6 3 |
| 7/7 | 1763 | 2 61 | 1 00 | 0.29 | 0 143 | 0 075 | 1.50 | A | 925 | 3 7 | 4 6 |
| 9/6 | 1841 | 2 47 | 0 95 | 0.23 | 0 156 | 0 065 | 0.01 | A | 925 | 12 3 | |
| 9/6 | 1842 | 2 48 | 0 96 | 0.24 | | | 0 01 | | | | |
| 9/6 | 1844 | 2 48 | 0.98 | 0.23 | | | 1 2 | A | | | |
| 9/6 | 1845 | 2.49 | 0 98 | 0 23 | | | 1.2 | A | 925 | 7 0 | |
| 9/6 | 1846 | 2.47 | 0 98 | 0 24 | | | 0 9 | A | 925 | 7.5 | |

^a All specimens heated to first-stage temperature at about the same rate. 2 2 hr. to 925° C.

PART I. GRAPHITIZATION

Determination of Graphitization Rate

Although the preliminary results were obtained by microscopic studies of specimens quenched after various treatments, the most valuable data were those obtained by measuring the expansion accompanying graphitization with a simple dilatometer. While it is probable that expansion is not directly proportional to the extent of graphitization, it is certain that cessation of expansion corresponds to complete graphitization⁴, at least within the sensitivity of the dilatometer used, which

⁴ A dilatometer measures change in length and is an accurate measure of a reaction only if the composition and density of the participating phases remain unchanged throughout the reaction. While the cessation of expansion remains an accurate index of the *completion* of graphitization, the amount of expansion at intermediate stages is not proportional to the amounts of cementite decomposed or graphite formed. The extent of the difference was shown by some chemical analyses run on specimens annealed at 925° C. for times that were equivalent to different proportions of the total dilatometer expansion. A specimen heated for the time corresponding to 100 per cent dilatometer expansion was microscopically found to be free from primary

would indicate a change of length accompanying the disappearance of about 0.5 per cent of the total amount of primary cementite present.

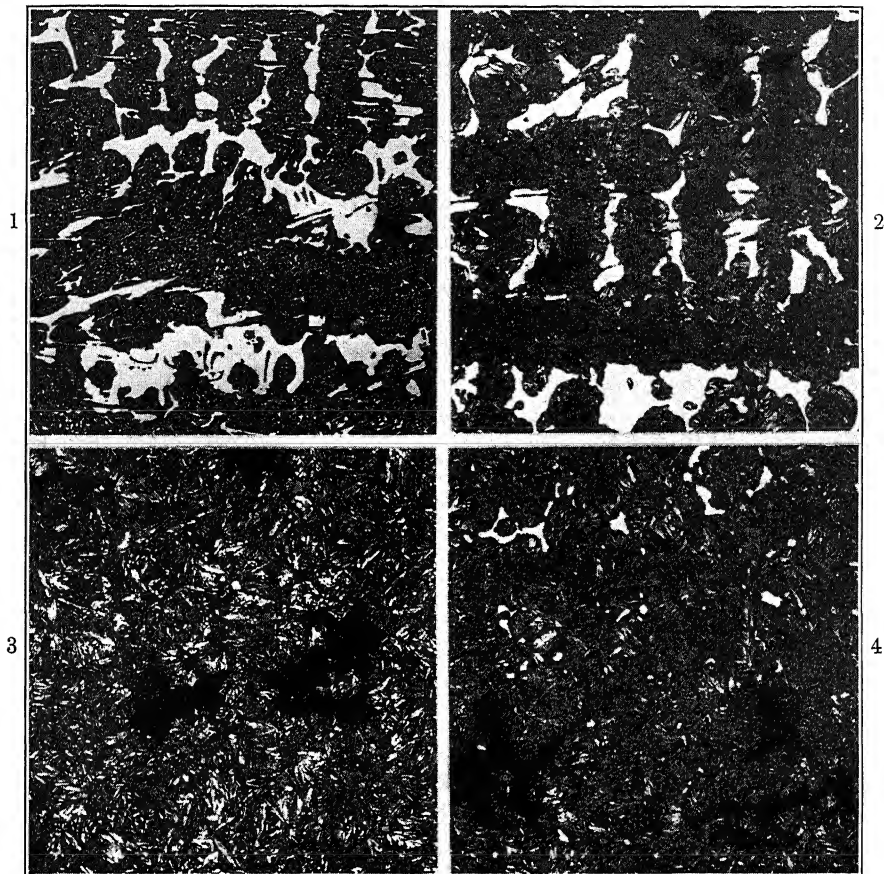


FIG. 1.—ALLOY 1652; 1.01 PER CENT SI, 1.3 PER CENT CU. HEATED TO 925° C. IN 2.7 HR. AND IMMEDIATELY QUENCHED. $\times 200$. (SEE TABLE 2.)

FIG. 2.—SAME AS FIG. 1, BUT HELD 61 MIN. AT 925° C.

EQUIVALENT TO 50 PER CENT OF FIRST-STAGE DILATOMETER EXPANSION. (SEE TABLE 2.)

FIG. 3.—SAME AS FIGS. 1 AND 2, BUT HELD 5.1 HR. AT 925° C.

EQUIVALENT TO 100 PER CENT OF FIRST-STAGE DILATOMETER EXPANSION.

FIG. 4.—ALLOY 1651. 1.0 PER CENT SI, 0.0 PER CENT CU. HEATED 5.1 HR. AT 925° C. (SEE FIG. 3.)

These specimens were reheated 0.5 hr. at 650° C. after quenching. Etched with 4 per cent nital.

It consisted of a silica tube and rod with an Ames gage graduated to 0.001 in. The specimens were 4.5 in. long. The dilatometer with

cementite and its combined carbon content was arbitrarily taken to correspond to 100 per cent graphitization. The amounts of intermediate graphite were calculated from the total combined carbon figures assuming oxidation to affect the graphite only. These data are summarized in Table 2 and some corresponding microstructures are shown in Figs. 1 to 4. It can be seen that the expansion lags considerably behind

TABLE 2.—*Comparison of Analytic with Dilatometric Measurements of Graphitization^a*

| Spec. No. | Time at 925° C., Hr. | Per Cent of Total First-stage Graphitization | |
|-----------|----------------------|--|----------------|
| | | By Analysis | By Dilatometer |
| 1652-M-6 | 0 | 1 | 0 |
| 1652-M-7 | 0 70 | 40 | 25 |
| 1652-M-8 | 1.02 | 66 | 50 |
| 1652-M-9 | 1.67 | 95 | 75 |
| 1652-M-10 | 5 17 | 100 | 100 |

^a See Table 1 for analysis of white iron. All specimens heated to 925° C. in 2.7 hr. Specimen M-6 was quenched immediately on reaching 925° C.

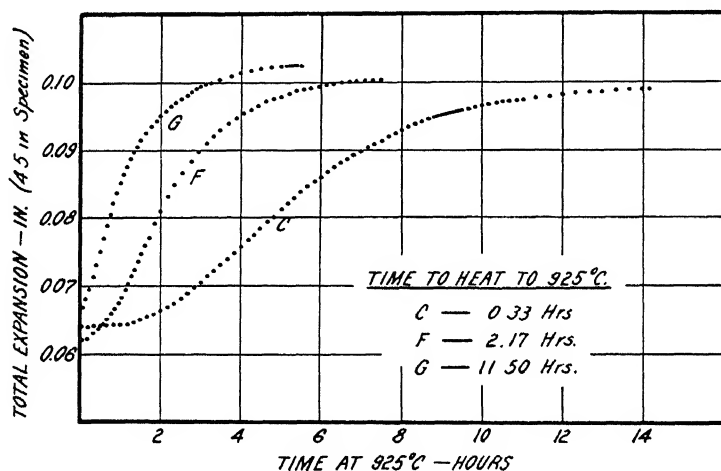


FIG. 5.—INFLUENCE OF SPEED OF HEATING TO 925° C. ON FIRST-STAGE GRAPHITIZATION AT 925° C.

Alloy 1651; 2.40 per cent C, 1.01 per cent Si, 0.0 per cent Cu.

the specimen in position was heated in a tube furnace on full current, and required about 130 min. to reach 925° C. The speed of heating is important and was kept approximately the same on all runs⁵.

graphitization as shown by analysis, and indicates a smaller amount than has actually been transformed.

⁵ The first few specimens examined showed that the graphitization of a white iron casting is not the simple mechanism that the literature leads one to believe, but that it is very sensitive to a number of factors. In some of the irons studied, particularly those melted in a small Detroit furnace, the furnace atmosphere appears to be of considerable importance, while in most irons, including those from commercial air-furnace heats, the speed of heating to temperature for first-stage graphitization is an important factor. The effect of heating speed is well shown by a number of dilatometer curves reproduced in Fig. 5 and by the more complete data of Table 3. The standard rate adopted for the studies summarized in the body of the paper

Readings were taken until expansion had ceased⁶, when, if second-stage graphitization was to be studied also, the specimen was cooled at a

TABLE 3.—*Influence of Heating Rate on Graphitization*

| Alloy No. | Composition, Per Cent | | Spec. No. | Speed of Heating to 925° C. ^b | Time at 925° C. for Completion of First-stage Graphitization, Hr. |
|-----------|-----------------------|---------|-------------------|--|---|
| | Copper | Silicon | | | |
| 1651 | 0 0 | 1 01 | C | Rapid | 14.0 |
| | | | D, F ^a | Slow | 7.2 |
| | | | G | Very slow | 5 5 |
| 1652 | 1.33 | 1.01 | A | Rapid | 7.0 |
| | | | C | Rapid | 6 5 |
| | | | D, F ^a | Slow | 4 7 |
| | | | E | Very slow | 3.7 |
| 1841 | 0.0 | 0.95 | B | Rapid | 18 6 |
| | | | A ^a | Slow | 12.3 |
| 1845 | 1.2 | 0.98 | B | Rapid | 9.2 |
| | | | A ^a | Slow | 7.0 |
| 1846 | 0.9 | 0.98 | B | Rapid | 9.1 |
| | | | A ^a | Slow | 7.5 |

^a See Table 1.

^b Rapid: Heated to 925° C. in about 20 min.

Slow: heated to 925° C. in 2.2 hr.

Very slow: heated to 925° C. in 11.3 hr. (controlled constant rate).

constant controlled rate of 1.3° C. per minute (80° C. per hour) until the critical point was passed and expansion due to the transformation had ceased. The temperature was then rapidly raised to 725° C., at which temperature all second-stage studies were made, and held constant until no further expansion occurred.

was free heating with the dilatometer furnace on full current, requiring about 2.2 hr. to reach 925° C.

Microscopic examination shows that in the specimens slowly heated to temperature the graphite is distributed in more numerous small particles, while the rapidly heated samples have rather few particles widely spaced and of larger size. The proportional saving of graphitizing time due to copper becomes less with the slower rate of heating. The greatest benefits of copper would be felt in short-cycle annealing practice.

⁶ To obviate the necessity of close personal attention on overnight runs a 16-mm. moving picture camera was adapted to take photographs of the gage and a watch placed alongside at suitable intervals. In cases where expansion ceased when the apparatus was unattended during the night, the specimen was, of course, held several hours after completion of graphitization. This time is indicated but not plotted in the graphitization curves. It seemed without effect on second-stage graphitization.

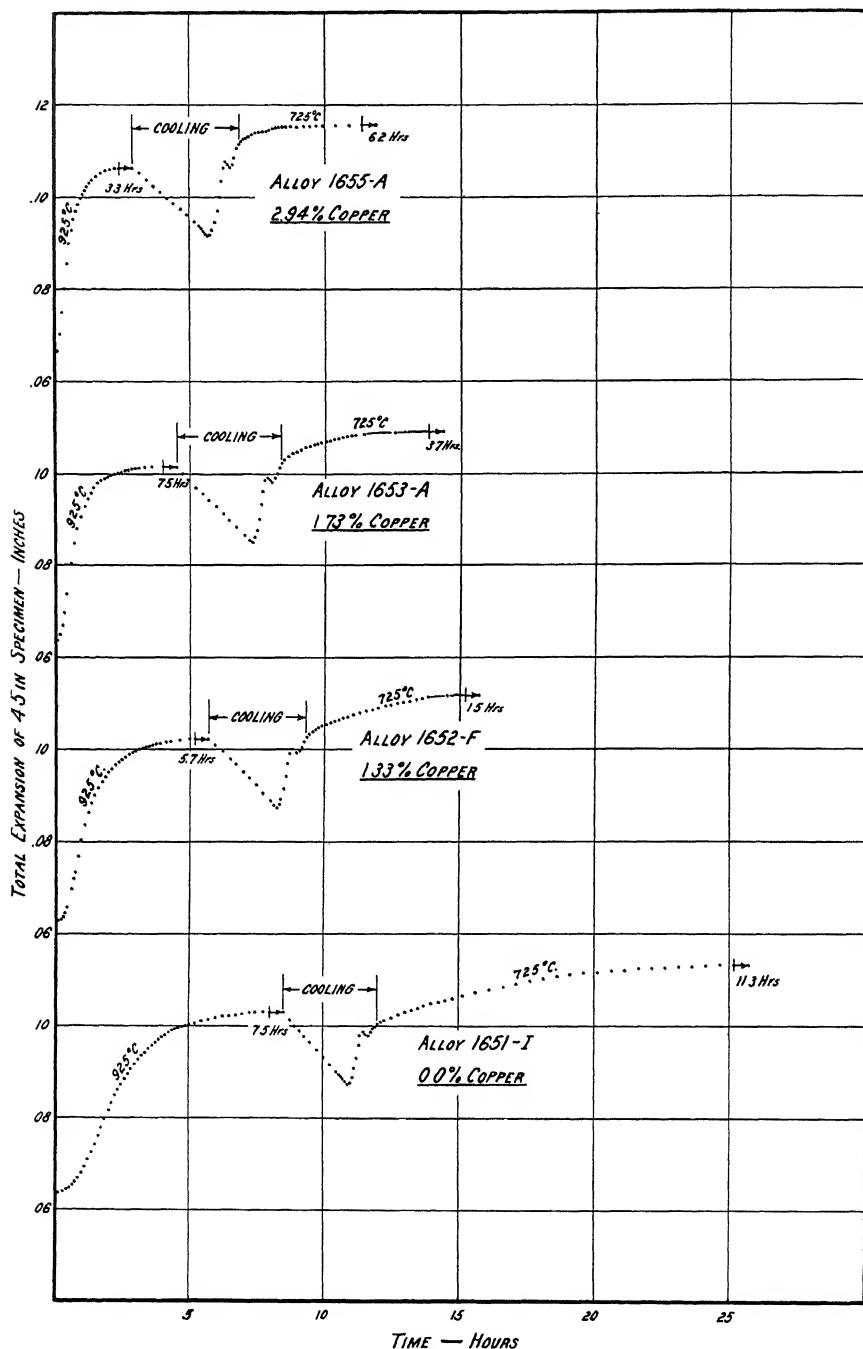


FIG. 6.—DILATOMETER CURVES SHOWING GRAPHITIZATION OF COMMERCIAL WHITE CAST IRONS.

Group 3/27; 2.40 per cent C, 1.01 per cent Si, Cu as noted. First stage at 925° C., second stage at 725° C. Cooling at 1.3° C. per minute.

Results

First-stage Graphitization.—Fig. 6 shows complete curves for expansion vs. time of four irons containing 2.40 per cent carbon and 1.01 per cent silicon, cast from the same heat but with various additions of copper. The time of heating to 925° C. (130 min.) was identical in all cases and

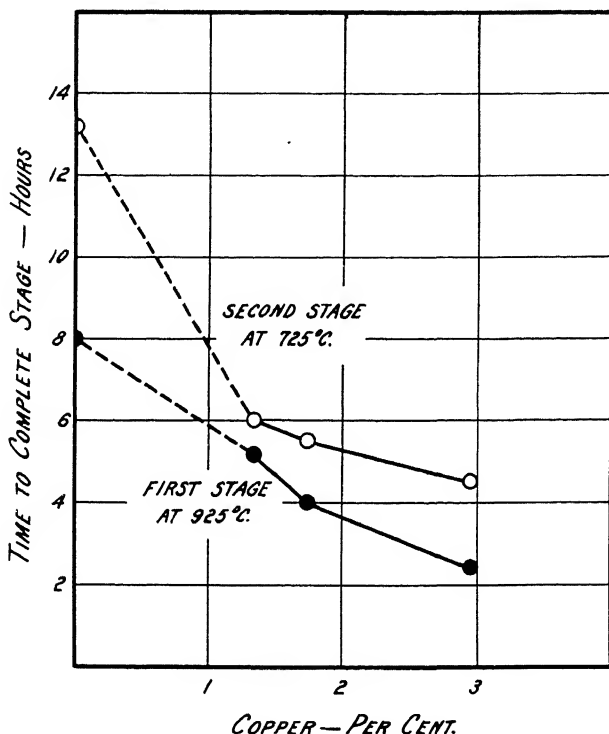


FIG. 7.—INFLUENCE OF COPPER CONTENT ON TIME FOR GRAPHITIZATION OF COMMERCIAL WHITE CAST IRONS.
Group 3/27; 2.40 per cent C, 1.01 per cent Si.

is omitted from the plotted curves. The specimens were held at 925° C. until it was certain that no further expansion was occurring, or longer if this occurred at night when the specimen was unattended. This additional time is not plotted, although it is indicated on the curves in order that the complete history of the specimens may be seen. The actual times for first-stage graphitization after reaching temperature are summarized in Table 1. Plotting the results against copper content, Fig. 7 shows more clearly the effect of copper in reducing graphitization time.

To eliminate the possibility of casting variables, three other groups of castings with slightly higher carbon content were obtained from another manufacturer at different times, and these also showed the

acceleration of annealing due to copper additions. The curves obtained on one group are shown in Fig. 8, plotted in the same manner as Fig. 6. All the results are summarized in Table 1, including some duplicate determinations, which show the reproducibility of the dilatometer results.

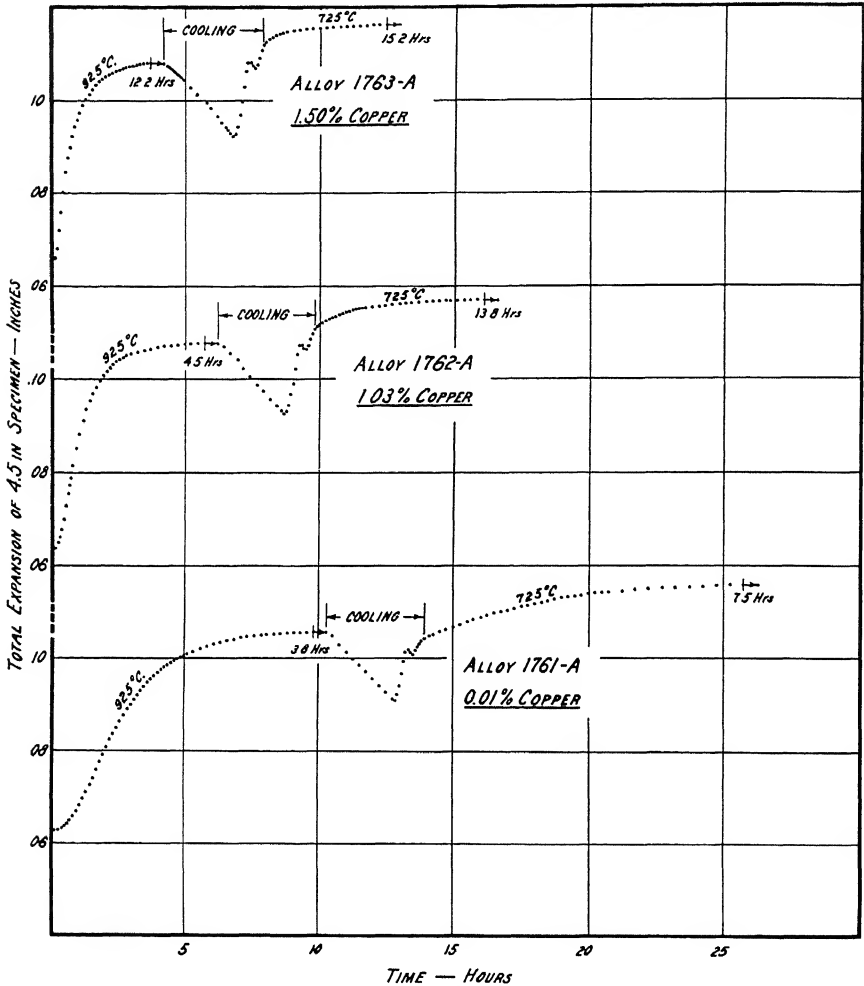


FIG. 8.—GRAPHITIZATION OF COMMERCIAL WHITE CAST IRONS.
Group 7/7; 2.61 per cent C, 1.00 per cent Si, Cu as noted.

Specimens of group 3/27 (alloys 1651 and 1652) were graphitized in the dilatometer at 890° C. and at 850° C., otherwise following the procedure used at 925° C. The data are included in Table 1 (specimens 1651-J and K, and 1652-G and H) and the first stage expansion of the two irons at 890° C. is compared in Fig. 9. The graphitization rate is less at the lower temperatures, but the accelerating effect of copper remains as great as at 925° C.

Second-stage Graphitization at Constant Temperature.—Many of the samples after the completion of first-stage graphitization were cooled through the critical point⁷ at a speed of 1.3° C. per minute (shown by microscopic examination to be sufficiently low to graphitize the proeutectoid cementite thrown out during cooling), and maintained at 725° C. until second-stage graphitization was complete, as shown by the cessation of expansion. This was checked by microscopic examination in many cases. Typical dilatometer readings are shown by the right-

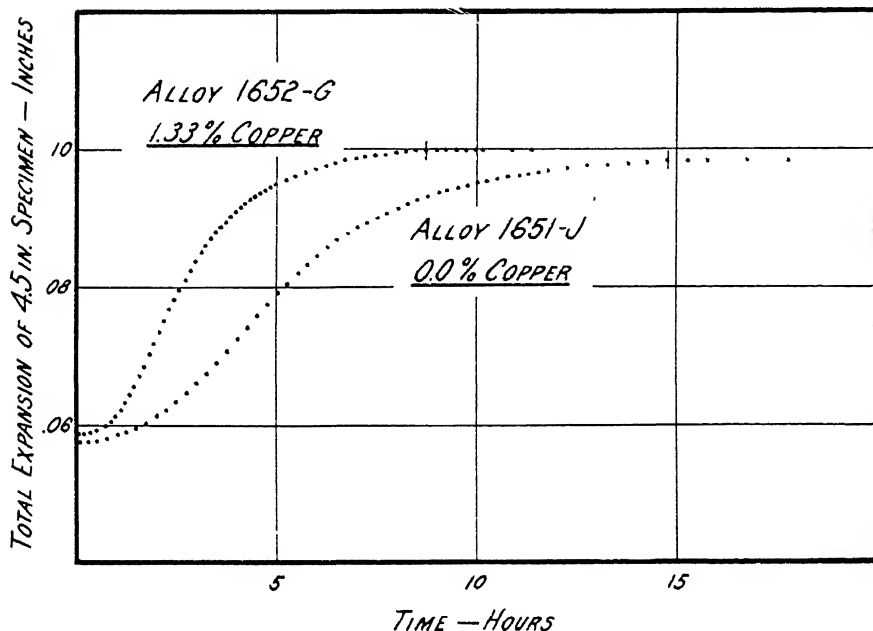


FIG. 9.—FIRST-STAGE GRAPHITIZATION AT 890° C. SAME IRONS AS IN FIG. 6.

hand portions of the curves in Figs. 6 and 8, and Table 1 and Fig. 7 summarize the results.

Copper has an effect in accelerating second-stage graphitization about equal to its effect on first stage. It is interesting to note that the specimens that were given first stage at 890° and 850° C. require a longer time for second stage at 725° C. than do the same irons given first-stage annealing at higher temperatures. This is probably connected with the size and distribution of the graphite particles, which are larger and less closely spaced after treatment at lower temperatures.

⁷ On account of lag the transformation did not occur at the true critical point but at a somewhat lower temperature. The specimens were cooled at the controlled rate until the transformation (expansion) was complete, when the temperature was rapidly raised to 725° C.

Second-stage Graphitization during Cooling.—In commercial annealing second-stage graphitization occurs during slow cooling rather than at a constant temperature. To ascertain whether copper has an accelerating effect under these conditions also, specimens of group 9/6 (alloys 1841, 1845 and 1846), after completion of first-stage graphitization at 925° C., were cooled to 750° C. (above the critical point) at a constant rate of 1.3° C. per minute, then to 650° C. at a constant rate of 12° C. per hour, and finally air-cooled to room temperature. The microstructures of these specimens are shown in Figs. 10 and 11.

The cooling rate used (12° C. per hour) is considerably higher than that used in commercial practice (4 to 8° C. per hour), and the copper-free specimen (Fig. 10) shows a considerable amount of pearlite. However, both of the copper-bearing specimens cooled at the same rate were substantially free from pearlite (Fig. 11, 0.9 per cent copper), indicating again the accelerating effect of copper on graphitization.

Microstructure.—The addition of copper had a slight but distinct effect in increasing the number and diminishing the size of graphite particles in an annealed iron. Figs. 3 and 4 as well as Figs. 10 and 11 show the effect of copper in accelerating graphitization. In the irons containing copper high magnification shows precipitated copper scattered throughout the ferrite grains (Fig. 12). At low powers this appears as an unresolved darkening of the ferrite.

PART II. PRECIPITATION-HARDENING

As is now well known, two steps are necessary in order to produce precipitation-hardening: (1) the production of a supersaturated solid solution by a "solution heat treatment" and cooling at a sufficiently rapid rate, and (2) the partial decomposition of this by heating at some lower temperature, the process being interrupted at some critical stage of the separation of the superfluous solute, a stage that may or may not correspond to actual precipitation as judged by the microscope or by change in lattice parameter. In copper-iron alloys and in the copper steels these treatments have been extensively studied by several investigators⁸⁻¹².

In copper steels heating to a temperature of about 750° C. or above dissolves sufficient copper to permit considerable subsequent precipitation-hardening after air cooling; in malleable iron the treatment is complicated by the re-solution of graphite, which occurs when the iron

⁸ Reference of footnote 1.

⁹ F. Nehl: *Stahl u. Eisen* (1930) **50**, 678.

¹⁰ H. Buchholz and W. Koster: *Stahl u. Eisen* (1930) **50**, 687.

¹¹ H. B. Kinnear: *Iron Age* (1931) **128**, 696, 820.

¹² J. T. Norton: *A.I.M.E. Tech. Pub.* 586 (1935).

is heated above the critical point and which limits treatment to a temperature below this unless some loss of ductility can be tolerated. The microstructure of an iron heated just into the critical range is shown

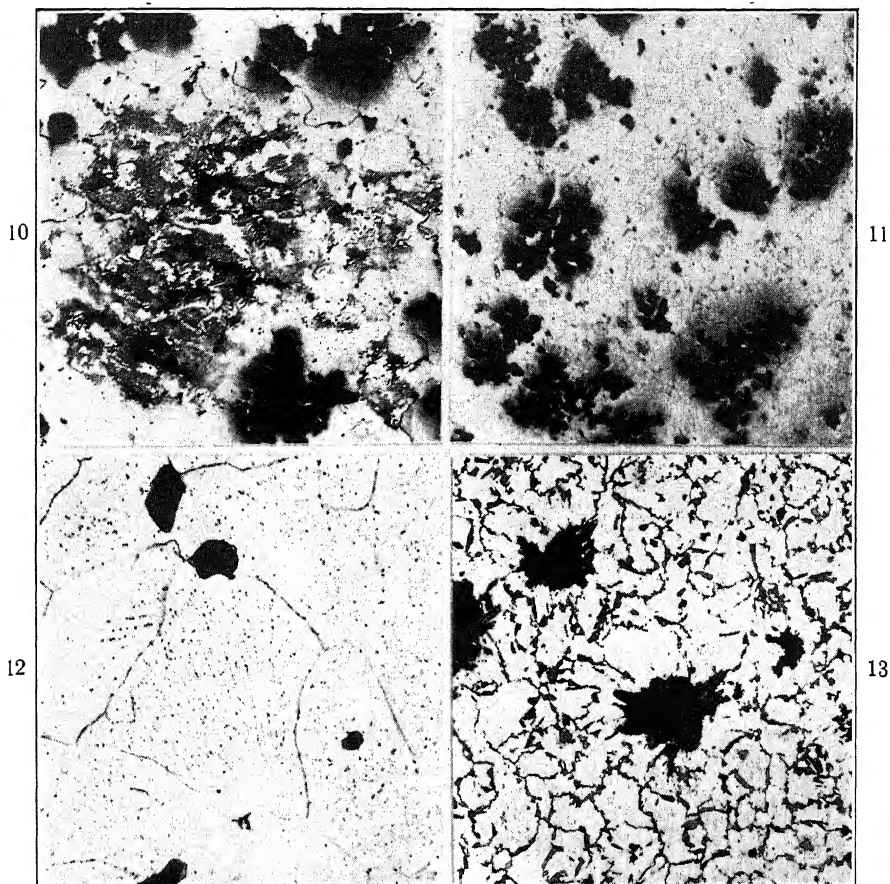


FIG. 10.—ALLOY 1841; 0.0 PER CENT CU. COOLED AFTER COMPLETE GRAPHITIZATION AT 925° C. TO 750° C. AT 1.3° C. PER MIN.; FURTHER COOLED TO 650° C. AT 12° C. PER HR.; AIR COOLED. $\times 100$.

FIG. 11.—ALLOY 1846. SAME HEAT AS FIG. 10 WITH 0.9 PER CENT CU. SAME TREATMENT AS FIG. 10. $\times 100$.

FIG. 12.—ALLOY 1652; 1.33 PER CENT CU. COMMERCIAL MALLEABLEIZED SPECIMEN, SHOWING COPPER PRECIPITATE. $\times 1000$.

FIG. 13.—ALLOY 1844; 1.2 PER CENT CU, 0.98 PER CENT SI. HELD 45 MINUTES AT 760° C.; AIR COOLED. $\times 200$.

in Fig. 13. Alloys with structure similar to this always have a partly white or mottled fracture. There is little change in microstructure below the critical point.

The critical points of a number of malleable irons containing copper as determined by microscopic examination of samples heated for 2 hr. at various temperatures spaced 5° C. apart are given in Table 4.

Treatment at temperatures below the critical point, which, as shown in Table 4, is lowered by the presence of copper, is insufficient to dissolve the maximum amount of copper that can be utilized for precipitation,

TABLE 4.—*Critical Points on Malleable Iron*
(Based on microstructure of specimens heated for 2 hr.)

| Alloy No. ^a | Analysis, Per Cent | | | Critical Temperature, Deg. C. |
|------------------------|--------------------|---------|--------|----------------------------------|
| | Carbon | Silicon | Copper | |
| 1651 | 2.40 | 1.01 | 0.0 | 755 |
| 1652 | 2.40 | 1.01 | 1.33 | 745 |
| 1653 | 2.40 | 1.01 | 1.73 | 743 |
| 1655 | 2.40 | 1.01 | 2.94 | 741 |
| 1731 | 2.64 | 0.91 | 0.05 | 752 |
| 1732 | 2.64 | 0.91 | 1.22 | 741 |
| 1761 | 2.61 | 1.00 | 0.01 | 752 |
| 1762 | 2.61 | 1.00 | 1.03 | 744 |
| 1763 | 2.61 | 1.00 | 1.50 | 742 |
| 1309 | 2.20 | 1.19 | 0.05 | 760 |
| 1310 | 2.27 | 1.27 | 0.67 | 755 |
| 1311 | 2.27 | 1.23 | 1.04 | 752 |
| 1312 | 2.28 | 1.19 | 1.53 | 750 |
| 1313 | 2.29 | 1.18 | 2.01 | 748 |

^a Alloys 1309–1313 were made in laboratory high-frequency furnace. Others are commercial air-furnace heats. All were fully malleableized before heating.

nevertheless it is sufficient to cause considerable improvement. This is shown by Fig. 14, wherein are plotted the results of duplicate tensile tests of a malleable iron heated for one hour at various temperatures, air-cooled and then reheated for 4 hr. at 500° C. to develop approximately maximum precipitation-hardening. A solution treatment at temperatures even as low as 700° C. permits some subsequent precipitation-hardening, and the amount steadily increases as the solution temperature rises. The strength of the iron in the normalized¹³ condition remains practically unchanged up to 750° C., but above this begins to increase on account of the solution of carbon. Fig. 15 shows results on an iron from the same heat containing no copper, and it will be seen that the reheated irons are somewhat inferior to the normalized ones and the change in direction of the curve due to carbon re-solution

¹³ The term "normalized" is used in this paper to signify air cooling following heating at any temperature in the neighborhood of the critical point. In its strict definition, "normalizing" refers solely to heating *above* the critical point, but it is adopted here to avoid the use of a long phrase.

occurs at a somewhat higher temperature than with the iron containing copper. In the copper iron the increase in yield point due to precipitation treatment is 10,000 to 15,000 lb. per sq. in. and the elongation decreases about 3 to 5 per cent. The total change in

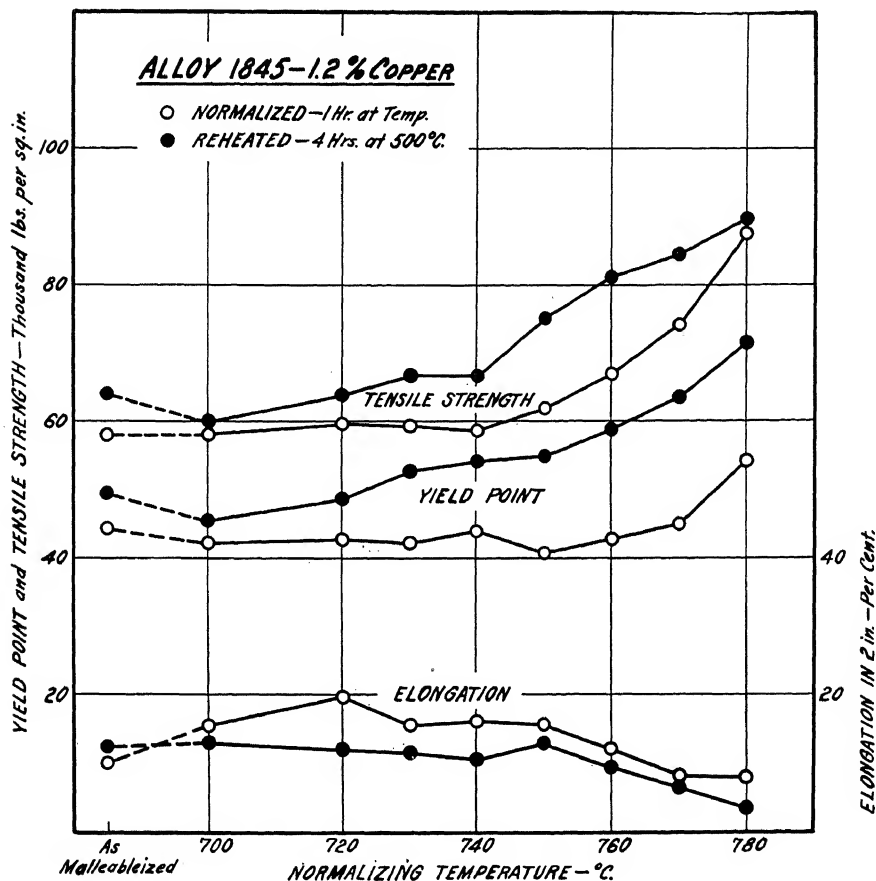


FIG. 14.—INFLUENCE OF NORMALIZING TEMPERATURE ON THE PRECIPITATION-HARDENING OF MALLEABLE IRON WITH 1.2 PER CENT COPPER.

yield point due to addition of copper and to the precipitation-hardening treatment is 20,000 lb. per sq. in., but the elongation is almost 10 per cent less.

If the castings are quenched instead of being air-cooled from temperatures near the critical point, there is a distinct increase in yield point and tensile strength for both irons, but this is lost when the copper-free iron is reheated, while the iron containing copper remains practically unchanged, since the precipitation of copper neutralizes the softening due to the other changes (Figs. 16 and 17).

It is interesting to note that copper-bearing iron in the malleableized condition shows a considerable improvement over the same iron without copper, an effect that is due partly to precipitation on cooling and partly to the retention of some copper in solid solution in the ferrite. All the

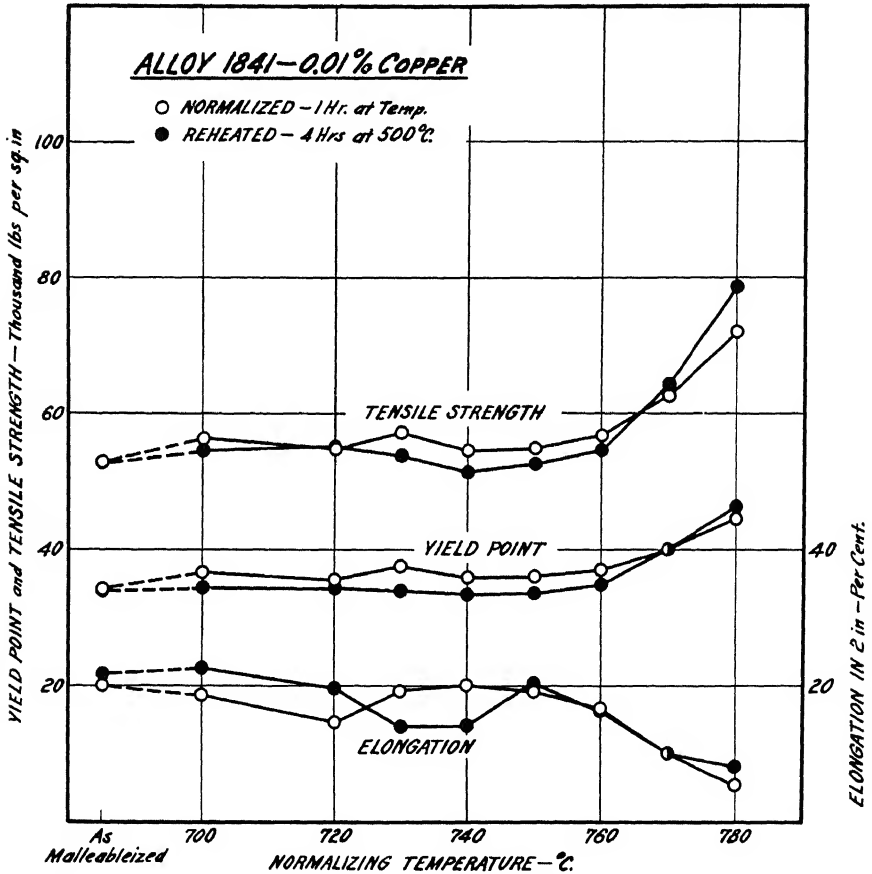


FIG. 15.—INFLUENCE OF NORMALIZING AND REHEATING ON PROPERTIES OF COPPER-FREE MALLEABLE IRON.

available copper is not precipitated by the malleableizing treatment, for some further improvement can be obtained on reheating the malleableized iron. The extent of this would depend, of course, on the temperature at which the bars were removed from the malleableizing oven and on the rate of cooling. It is possible to perform the precipitation treatment without any intermediate cooling to room temperatures throughout the entire process. After malleablization is complete, the temperature is raised to about 740° C., the castings withdrawn and air-cooled to 500° C.,

held at this temperature for about 4 hr., and then finally air-cooled,

The time of the solution treatment is comparatively unimportant (Figs. 18 and 19), while the temperature and time of reheating may be varied over wide limits without greatly affecting the results obtained.

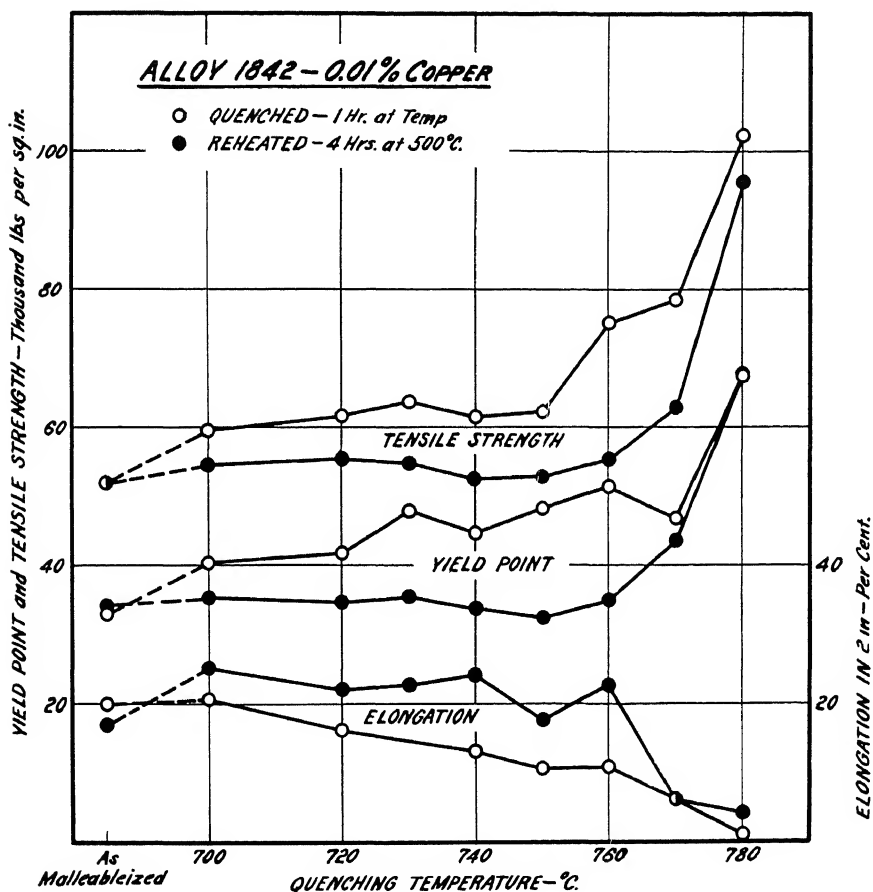


FIG. 16.—INFLUENCE OF QUENCHING TEMPERATURE ON PROPERTIES OF COPPER-FREE MALLEABLE IRON.

as may be seen from Figs. 20 and 21. Perhaps the best combination of properties in a 1 per cent copper iron is obtained by solution heat treatment for about 1 hr. at 740° C. followed by air cooling and reheating for 3 to 6 hr. at 500° C. Higher solution temperatures give greater strength but at a loss of ductility.

Table 5 shows typical properties that might be expected from a malleable iron containing copper, although naturally these will vary considerably with the quality of the base iron.

TABLE 5.—*Tensile Properties of Heat-treated Malleable Iron Containing 1.2 Per Cent Cu, 2.5 Per Cent C, 1.0 Per Cent Si*

| Treatment | Yield Point, Lb. per Sq. In. | Tensile Strength, Lb. per Sq. In. | Elongation on 2 In., Per Cent |
|--|---------------------------------|---|-------------------------------------|
| As malleableized | 45,000 | 59,000 | 14 |
| Normalized 740° C. 1 hr | 43,000 | 58,000 | 15 |
| Normalized 760° C. 1 hr. and reheated 500° 6 hr. | 54,000 | 67,000 | 12 |
| Normalized 760° C. 1 hr | 43,000 | 67,000 | 12 |
| Normalized 760° C. 1 hr. and reheated 500° 5 hr. | 58,000 | 80,000 | 7 |

SUMMARY

By dilatometric and other methods the addition of copper has been found to accelerate both first-stage and second-stage graphitization of

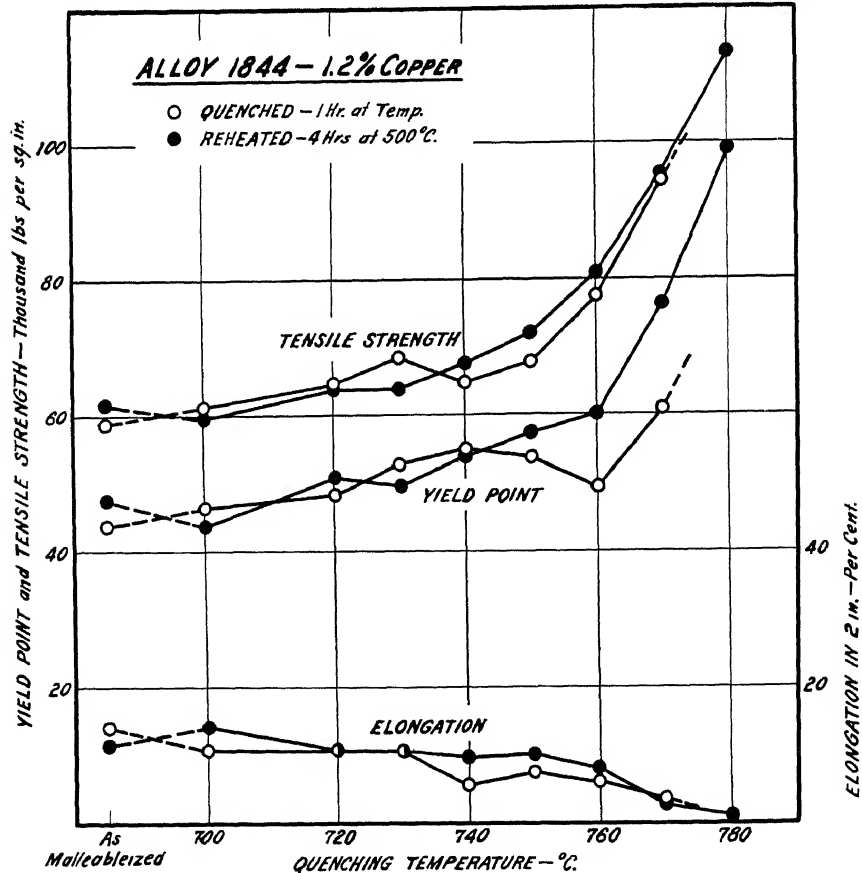


FIG. 17.—INFLUENCE OF QUENCHING TEMPERATURE AND REHEATING ON MALLEABLE IRON CONTAINING 1.2 PER CENT CU.

white cast iron. The effect is roughly proportional to the amount of copper added and 1 per cent of copper results in a reduction of graphitization time by about 50 per cent, although this is affected by the rate of heating and other factors.

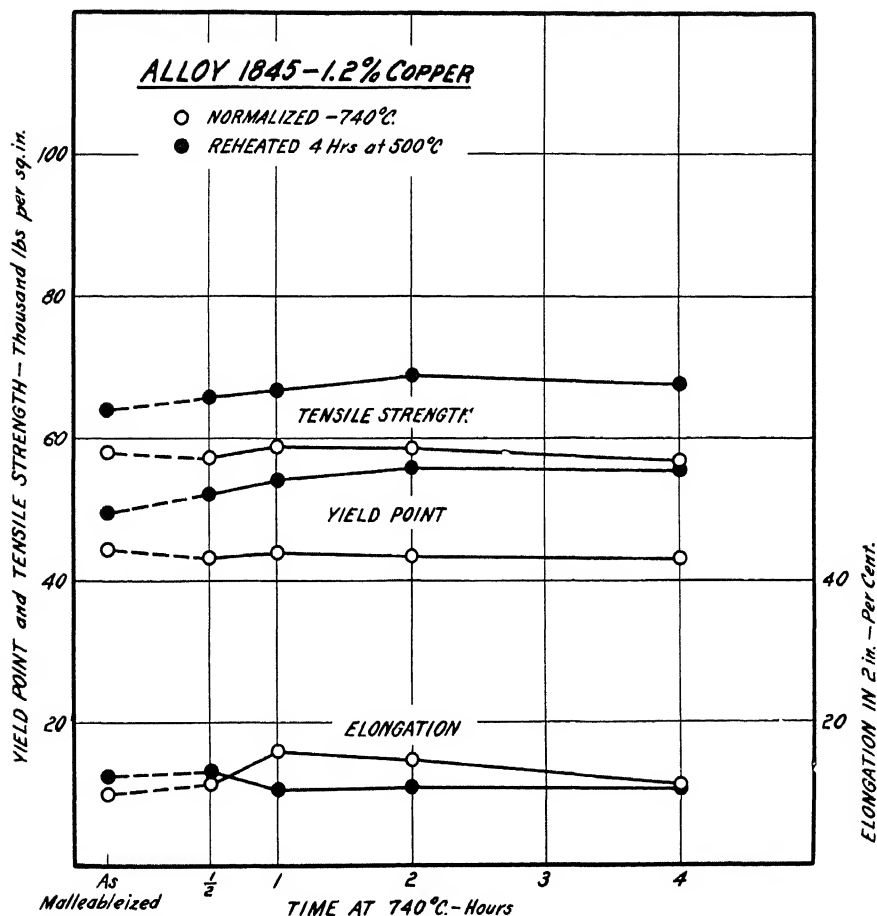


FIG. 18.—INFLUENCE OF TIME OF SOLUTION HEAT TREATMENT AT 740° C. ON PRECIPITATION-HARDENING OF MALLEABLE IRON CONTAINING 1.2 PER CENT COPPER

The addition of 1 to 1.5 per cent of copper increases the yield point of malleableized iron to the extent of about 10,000 lb. per sq. in., and a further gain of 10 to 15,000 lb. per sq. in. can be obtained by subjecting the castings to a precipitation-hardening treatment. This consists of heating to a temperature closely below the critical point, air cooling and reheating at about 500° C. The increase in tensile strength is accompanied by some loss in ductility.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to the following companies and individuals: The Copper and Brass Research Association for its sponsorship and continued support; The American Brass Company for providing laboratory facilities; the Columbus Malleable Iron

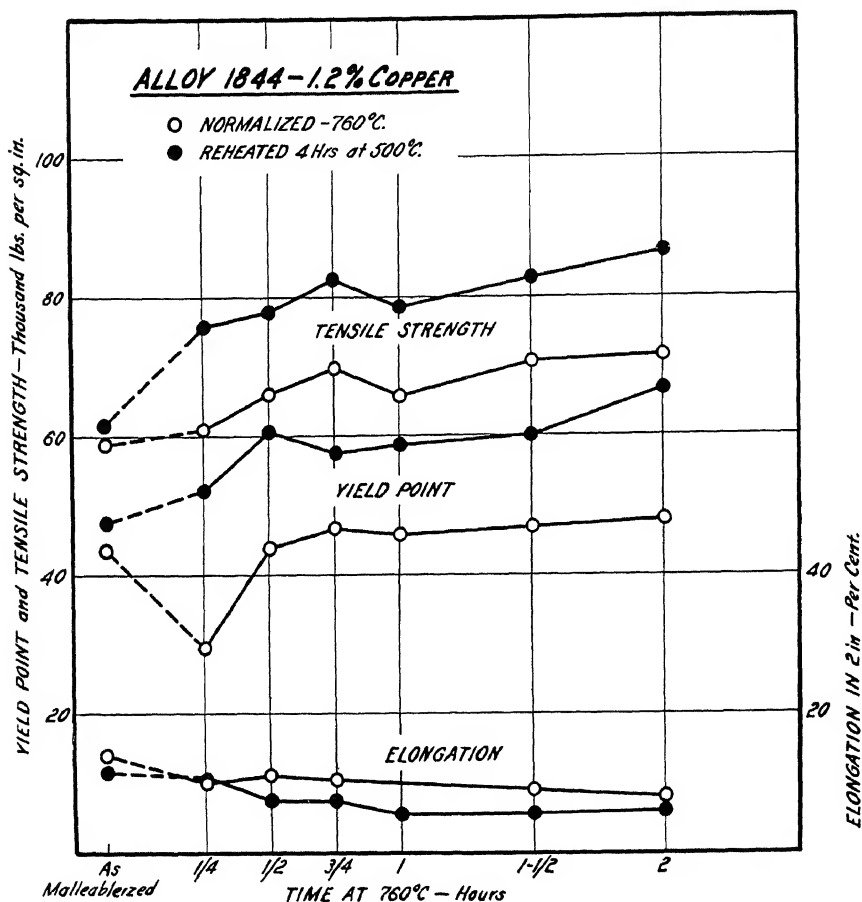


FIG. 19.—EFFECT OF TIME OF SOLUTION HEAT TREATMENT AT 760° C. ON PRECIPITATION-HARDENING OF MALLEABLE IRON CONTAINING 1.2 PER CENT COPPER.

Company and the Ohio Malleable Iron Company for providing the commercial castings; Dr. C. H. Lorig and others in the Battelle Memorial Institute for supervising the casting of the iron, for performing analyses and for help in other ways; and to several individuals in the laboratory of The American Brass Company for performing the tensile tests and many analyses.

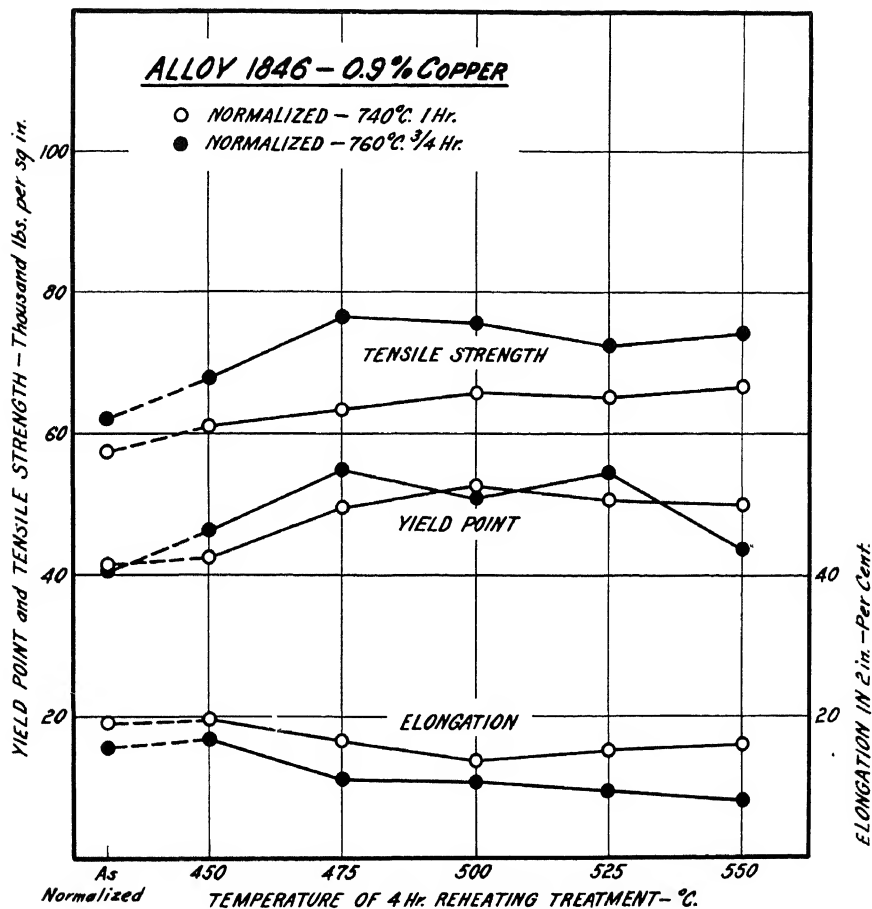


FIG. 20.—INFLUENCE OF TEMPERATURE OF REHEATING ON PRECIPITATION-HARDENING OF MALLEABLE IRON CONTAINING COPPER; PREVIOUSLY NORMALIZED FROM 740° OR 760° C.

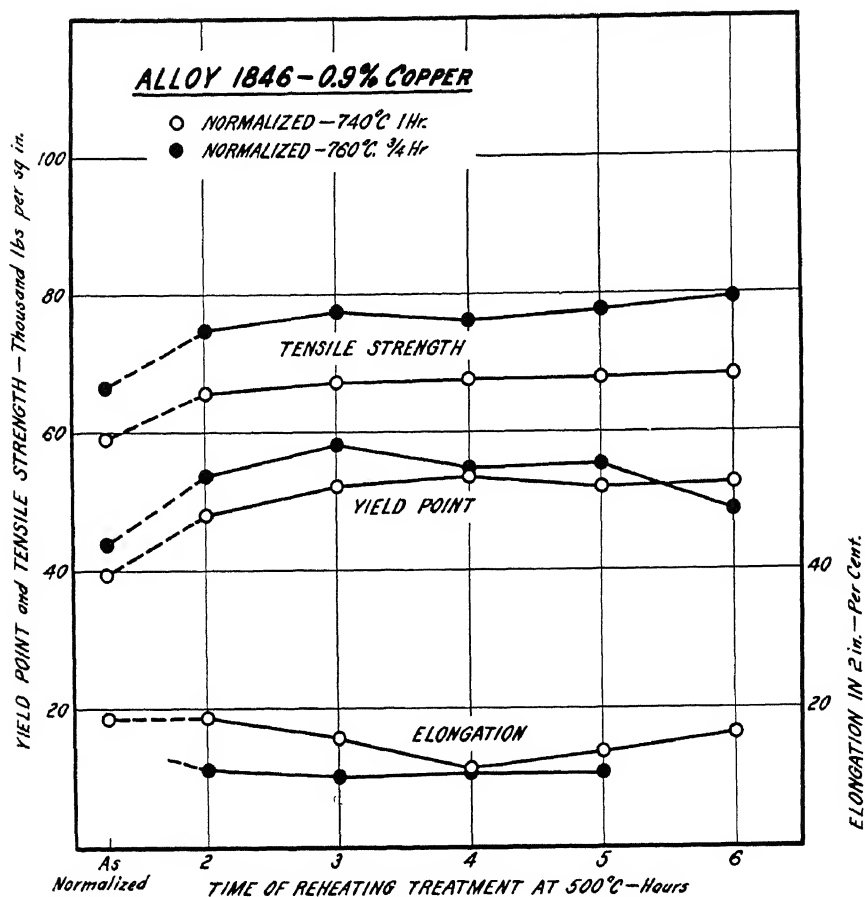


FIG. 21.—INFLUENCE OF TIME OF REHEATING AT 500° C. ON PRECIPITATION-HARDENING OF MALLEABLE IRON CONTAINING 0.9 PER CENT CU, PREVIOUSLY AIR-COOLED FROM 740° OR 760° C.

DISCUSSION

(George B. Waterhouse presiding)

A. L. BOEGEHOLD,* Detroit, Mich.—The authors have shown that malleable iron to which copper has been added annealed more rapidly than iron not so treated. They give no data to show that due consideration has been given to other factors that might have been responsible for the result obtained. Obviously the addition of 1 to 2 per cent of copper to molten iron will cool it considerably, causing a large difference in casting temperature between irons with and without copper additions.

Was the iron without copper cooled to the same casting temperature as the iron to which copper was added, and, likewise, was the iron containing 1.31 per cent copper cast at the same temperature as the iron containing 2.94 per cent copper? Since no mention is made of such precautions, it gives the impression that the importance of such measures were not appreciated. The chilling of iron in the ladle by addition of copper causes more rapid solidification of the iron in the mold just as casting in lighter sections does, or as chilling in the ladle with white iron scrap.

We have observed that by increasing the rate of solidification we can increase the rate of first-stage graphitization as much as shown in Table 3 without the addition of copper. This increased rate is due to the closer packing of the temper carbon spots, which results from faster solidification caused by any one of a variety of methods.

I have observed the effect of rate of heating upon size of temper carbon spots and their distribution and the consequent increase in speed of graphitization. For comparison with data in Table 3, an iron that required 25 hr. for the completion of first-stage graphitization when heated to 1700° F. at 225° F. per hour, required only 8 hr. when heated at 30° F. per hour. The same iron, when cast in a light section, required only 3½ hr. when heated at 30° F. per hour.

The quantitative evaluation of the effect of copper upon graphitization must be made therefore with due consideration given to the influence of solidification rate.

The statement made in footnote 5, that "the proportional saving of graphitizing time *due to copper* becomes *less* with the slower rate of heating," strengthens my suspicion that faster cooling rate is responsible for this result rather than copper, because we have observed that the proportional saving of graphitizing time *due to faster solidification* becomes *less* with the slower rate of heating.

It is noted that experiments were all conducted on a ⅝-in. round casting. In a casting of this size we could speed up graphitization by merely adding silicon, which is more potent than copper. The same reason that prevents us from doing it would apply to the use of appreciable copper additions. How much copper can be added without obtaining primary graphite in a 2½-in. round test bar, which is a size commonly cast to check the quality of the "hard iron"?

E. W. PALMER.—I am not exactly qualified to speak on the casting of these bars, since they were done under the direction of Dr. Lorig, of Battelle Memorial Institute. It is my understanding that the casting temperature was carefully controlled throughout. I am quite sure that there was a greater difference in temperature between various flasks of the same composition than there was between the copper-free and the copper-bearing irons.

Our work was limited to ⅝-in. diameter casting, and we have no data bearing at all on bars 2½ in. in diameter; but it has been determined in a qualitative sort of way that 1 per cent copper is equivalent to only 0.10 per cent silicon in the promotion of primary graphitization. For this reason it seems that copper still has some

* Metallurgist, General Motors Research Laboratories.

advantage as an addition agent even though similar results may be obtained by increasing the silicon content.

H. A. SCHWARTZ,* Cleveland, Ohio (written discussion).—From a fairly considerable background of experimentation the present commentator is able to confirm in general terms the conclusions of Messrs. Smith and Palmer as to the effect of copper on the physical properties of malleable cast iron and the relation of this effect to the heat-treatment subsequent to complete graphitization. He has already said in a discussion of the authors' second reference that this investigation is industrially a more interesting development in the malleable foundryman's art.

From a scientific viewpoint the investigation of the present authors adds considerably to the information gathered in 1926 by Sawamura¹⁴ on the same subject. Messrs. Smith and Palmer have investigated quantitatively the accelerating effect of copper much more effectively than their Japanese predecessors. Their observation that the dilation of the specimen does not bear a simple linear quantitative relation to the graphite formed is, to the present commentator, the most interesting feature of their discussion, even though it is but incidentally related to their major thesis.

It is hoped to investigate their observations in greater detail in an attempt to furnish a quantitative explanation for the changes of density to which the authors point. Pending such a detailed study it may be well to point here to the fact that as shown by Schwartz, Van Horn and Junge¹⁵, the carbide phase of white cast iron changes materially in carbon content at such temperatures as were used in the investigation by Messrs. Smith and Palmer.

It would seem at first glance reasonable that since the carbon content of cementite increases while its lattice parameter is not so greatly altered it is likely that the cementite phase is relatively denser at 925° C. than it would have been had its composition remained unaltered. It must be remembered also that if there are two solutions of carbon in iron, one additive and the other substitutional, the two will certainly have different densities. It is not particularly unlikely that the substitutional solid solution should be less dense than the additive solid solution, which is thoroughly known as austenite. If, therefore, there should be a progressive change from one type of solid solution to another, it is fairly reasonable that the density of metal might in the later stages decrease more rapidly than would be indicated by the amount of graphite separated. Attempts are being made at the writer's instigation to examine the possible existence of two solutions by X-ray spectrometric methods. If any success can be had by the investigator who has kindly interested himself in this problem, it may be possible to shed a more convincing light upon the reason for the present authors' observations. For the present we must confine ourselves merely to the pointing out what appears to be possible satisfactory correlation between the observations of Messrs. Smith and Palmer and what is already known with respect to the phase changes during graphitization.

The commentator further hopes that not many readers will conclude from the literature, as did the present authors, that graphitization is a relatively simple matter. Leaving aside all such variations as gaseous environment, changes of chemical composition and so on, the mere problem of the rate of deposition of graphite as an expression of the combination of the form of graphite nuclei and of crystalline velocity in graphite, all in the light of the possible migratory rate of carbon atoms in iron, is, as the present authors have correctly observed, a matter of very great complexity.

* Manager of Research, National Malleable and Steel Castings Co.

¹⁴ Influence of the Various Elements on the Graphitization in Cast Iron. College of Engineering, Kyoto Imperial Univ. *Mem.* (1926) 4, No. 4.

¹⁵ Transformation in the Carbide Phase during Graphitization. *Trans. Amer. Soc. Steel Treat.* (1933) 21, 463.

C. S. SMITH (written discussion).—The acceleration of graphitization due to copper, while large, is no larger than that which may be obtained by some other methods; for example, by increasing the silicon content, by superheating, or by rapid chilling of the casting. We feel, however, that the effect is much greater than any that might have been caused by the variation of pouring temperature that occurred in our experiments.

Copper will prove an advantageous addition from the standpoint of accelerating the malleabilizing anneal only if it has less effect on primary graphitization than a change of one of the other factors which would produce the same reduction of malleabilizing time. The data showing the effect of copper on primary graphitization is very incomplete and inconclusive. Some of our early experiments even showed that copper would inhibit mottling, but the overwhelming evidence is to the contrary.

Similarly, the change in properties due to a precipitation-hardening treatment on malleable iron containing copper is not great and equally good properties are obtainable by other more complicated heat-treatments on copper-free malleable iron. Under some conditions precipitation-hardening will be commercially useful. We believe that it is for the malleable-iron industry to weigh the improvements accruing from the use of copper against those obtainable by other methods and to decide whether copper is really an economical addition to malleable iron.

We appreciate Dr. Schwartz' remarks and are gratified that our results are in agreement with his other data.

Solubility of Copper in Iron, and Lattice Changes during Aging

BY JOHN T. NORTON,* ASSOCIATE MEMBER A.I.M.E.

(New York Meeting, February, 1935)

FOR many years the copper-bearing steels have been of considerable interest to the metallurgist because of their corrosion-resistant properties. More recently the discovery of their definite age-hardening characteristics has focused attention on them again. In a recent paper, Smith and Palmer⁽¹⁾† have given an admirable description of the behavior of a considerable number of steels of this type and a study of their results suggests two questions of a more or less fundamental sort.

In the first place, it has been plainly shown that the hardening effect of added copper does not increase up to the maximum solubility of copper in iron as given by earlier investigators, but reaches its greatest value considerably below this point. This fact suggests that either the solubility is not so great as previous investigators have stated, or that the age-hardening mechanism is not the simple precipitation phenomenon that has been postulated.

In the second place, the nature of the aging mechanism in this particular system should be determined. Recent developments in the study of age-hardening processes have shown that the increase of hardness is often, but not always, accompanied by precipitation and the action of a particular system is not predictable on the basis of its components or type of phase diagram. It would be of considerable interest to study the aging of the iron-rich iron-copper alloys in detail. One would like to know whether the aging mechanism is different at high and low aging temperatures, and whether the extreme sluggishness of the system may perhaps represent some new type of aging process.

The experiments to be described were carried out in an endeavor to answer these questions. Obviously, in such experiments it is important to confine the hardening effect to the single element, copper, so that iron and copper of high purity must be used in the preparation of specimens. An observation of lattice changes during the aging process, correlated with the hardness changes, seems to be the best available method of

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† References are at the end of the paper.

studying the hardening mechanism. Similarly, the solubility relations are best determined by a study of lattice changes. Such studies can be made directly only by means of X-rays.

PREVIOUS WORK

The most careful attempt to determine the alpha-phase boundary at the iron-rich end of the iron-copper system seems to be that of Buchholz and Köster.⁽²⁾ The electrical resistivity method was used and their results are shown in Fig. 2. As far as the writer is aware, no previous observations of lattice changes during aging have been made.

AUTHOR'S INVESTIGATION

Materials Used.—The alloys used in the present investigation were made by melting iron and copper of high purity together in vacuum in a high-frequency furnace. The iron was a purified electrolytic product obtained from the Westinghouse Electric and Manufacturing Co., for which the following analysis is given: C, 0.00125 per cent; Si, 0.002; S, 0.008; Mn, 0.004; Al, 0.004; P, 0.002; Fe, 99.97 per cent.

The copper was a sample of oxygen-free high-conductivity copper (brand OFHC), described by Webster, Christie and Pratt.⁽³⁾ In this material, the total impurities run less than 0.02 per cent. The ingots were remelted to insure a homogeneous composition and were annealed in dry hydrogen at 900° C. (1650° F.) for 100 hr. Analysis showed the composition listed in Table 1.

TABLE 1.—*Analysis of Alloys*

| Alloy | Weight Per Cent Copper | Alloy | Weight Per Cent Copper |
|-------|------------------------|-------|------------------------|
| A | 0 | E | 0.75 |
| B | 0.25 | F | 2.06 |
| C | 0.31 | G | 3.39 |
| D | 0.44 | | |

X-ray Methods.—The lattice constants of the various specimens were determined by the back-reflection method, using the plane surface of a solid sample. Proper preparation of the surface by polishing and etching resulted in a clearly resolved alpha doublet. Chromium radiation was used. The values of the cube edge are certainly reproducible to $\pm 0.0002\text{\AA}$., while if several films are averaged this figure can be materially improved.

In a recent paper, Phillips and Brick⁽⁴⁾ discussed the influence of lattice strains resulting from quenching on the value of the lattice

parameter. No evidence of such an effect has been observed in the present work. The diffraction lines were very sharp in all cases and no

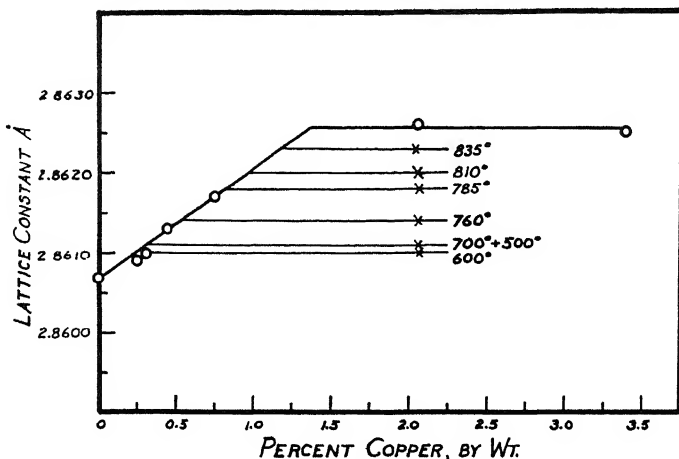


FIG. 1.—RELATION OF COMPOSITION AND LATTICE PARAMETER FOR IRON-RICH SOLID SOLUTION.

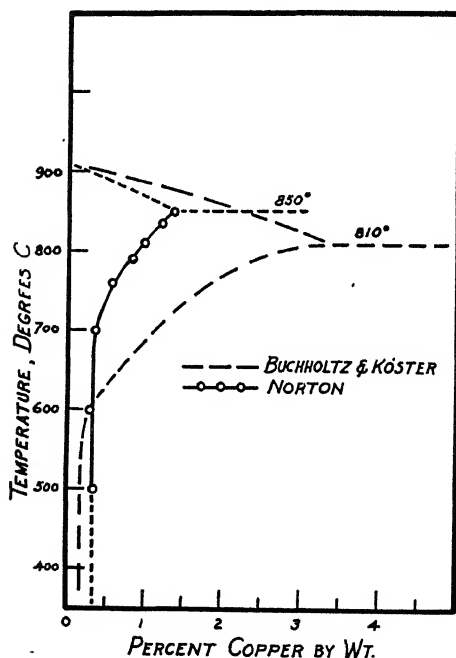


FIG. 2.—SOLUBILITY OF COPPER IN IRON.

abnormally small values for the completely precipitated alloys were found. There seems no reason to believe that this factor is a source of error in the results, although the possibility has not been entirely eliminated.

Determination of Solubility.—The solid solubility of copper in iron was determined in the conventional manner. Heating curves showed the eutectoid transformation to be between 855°C . (1570°F .) and 860°C . (1580°F .). The complete series of alloys was quenched from 860°C . (1580°F .), and the lattice constants were measured. This gave the curve relating composition and parameter shown in Fig. 1. It indicates the maximum solubility to be about 1.4 per cent of copper by weight.

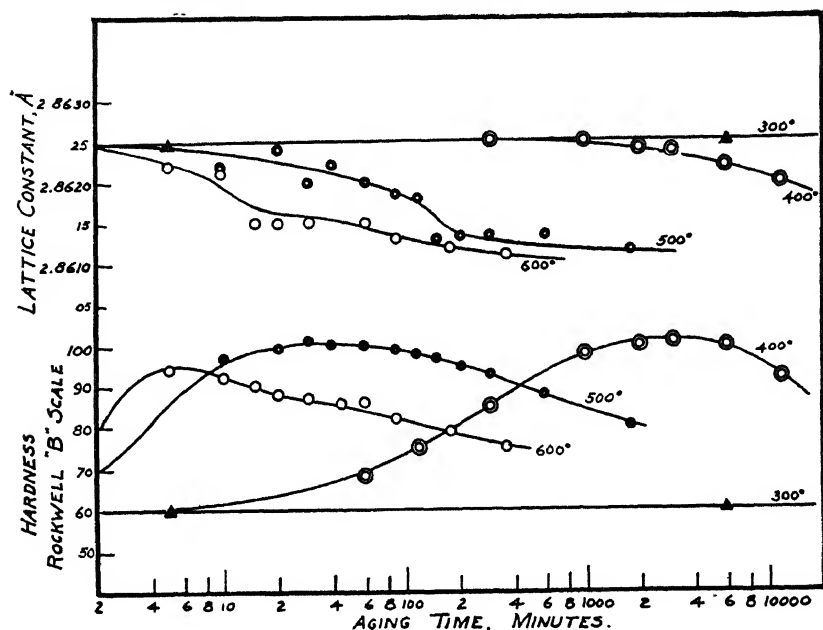


FIG. 3.—CHANGES IN HARDNESS AND LATTICE PARAMETER WITH TIME OF AGING AT DIFFERENT TEMPERATURES.

An alloy of copper content somewhat greater than maximum solubility (alloy F) was used to determine the solubility curve. The sample was quenched from 860°C . (1580°F .) and then aged for a long period at the temperatures indicated by the crosses in Fig. 1. The aging was continued until the parameter became constant, indicating equilibrium at that temperature. Fig. 2 shows the solubility curve obtained compared with the best previous work.

Aging Experiments.—The primary purpose of the aging experiments was to correlate the changes in lattice parameter with the changes in hardness as the aging proceeded.

The sample having a copper content slightly greater than the maximum solubility (alloy F) was used in the aging experiments. The sample was given a solution heat treatment at 860°C . (1580°F .), quenched, and then aged at the desired temperature. At suitable intervals, the aging was interrupted by quenching in order to make the X-ray and

hardness measurements. Experiments showed that intermittent and continuous aging gave equivalent results. Recent results by Phillips and Brick⁽⁴⁾ confirm this. Fig. 3 shows the results of the aging at various temperatures. At 300° C. (570° F.), no increase in hardness or change in parameter was detectable. At 700° C. (1290° F.), the hardness increased so rapidly that no suitable measurements could be made.

The saturated alloy had a lattice-parameter value of 2.8625Å., while, after complete precipitation, the value was 2.8611Å. The maximum hardness occurred at all aging temperatures at about 2.8621Å., which corresponds to a precipitation of between a fourth and a fifth of the available copper.

DISCUSSION OF RESULTS

Solubility

The maximum solubility of copper in iron, as can be seen from Fig. 2, is considerably lower than the results of earlier work. The best previous determination is that of Buchholtz and Köster,⁽²⁾ who employed electrical resistivity measurements. Their results indicate a eutectoid temperature of 810° C. (1490° F.). While no very precise measurement of this transformation was attempted, the value from the present experiments is tentatively set at 850° C. (1560° F.), which is in good agreement with the results of Smith and Palmer⁽¹⁾ on a copper steel containing 0.011 per cent carbon. Buchholtz and Köster⁽²⁾ show a maximum solubility of 3.3 per cent copper by weight as compared with a value of 1.4 per cent found in these experiments. The present results show a constant solubility of 0.35 per cent copper below about 650° C. (1200° F.), while the earlier results show a minimum value of 0.20 per cent. Smith and Palmer⁽¹⁾ show that low-carbon copper steels begin to show age-hardening at 0.7 per cent copper by weight, and that the hardening effect reaches its maximum at 1.5 per cent copper. This agrees well with the solubility curve resulting from the present experiments. No reason for the wide discrepancy between the earlier results and those reported here is obvious. Quenching strains may play some small part and experiments with powder samples are planned, which should settle this point.

Age-hardening

A considerable number of experiments upon duralumin and related alloys have resulted in the development of a fairly satisfactory theory of their behavior during age-hardening. It is of interest to examine the iron-copper alloys in the same way to see whether they obey similar general laws or whether some new mechanism of hardening must be developed to explain the experimental evidence.

On the basis of the behavior of duralumin, two definite factors are recognized, which probably contribute to the increase in hardness of iron-copper alloys. One of these factors is associated with the rearrangement that is believed to take place in the supersaturated solid solution prior to actual precipitation. The exact nature of this rearrangement is not known but is generally believed to be a migration of copper atoms to form tiny groups or "knots."⁽⁵⁾ The copper atoms still occupy lattice points of the iron lattice but form groups which must approximate very closely the mutual positions they will have in the copper crystal that is to be precipitated. Such a rearrangement does not cause a change in lattice parameter, as shown by X-ray diffraction, which must mean that the copper atoms are still on the points of the iron lattice, but the lattice is undoubtedly distorted in some irregular way and this has an influence on resistance to deformation or hardness. This type of lattice distortion is not necessarily accompanied by a broadening of the diffraction lines.

The other factor is the hardening effect due to the formation of a finely divided precipitate. For present purposes, precipitation is considered as a transformation that produces a change in the composition of the solid solution, a change that is indicated by a change in lattice parameter. In the past, precipitation-hardening has been assigned a major role, probably because the precipitated particles can sometimes be seen under the microscope while the "knots" cannot. In regard to duralumin, it has been shown that both of these factors are operative but that their relative contributions to the hardness depend markedly upon the temperature of aging. At room temperature the precipitation is entirely suppressed while at 300° C. (570° F.) it becomes the important factor. At 200° C. (390° F.), two hardness maxima are observed, one due to "knot" formation and the other to precipitation.

Examination of the iron-copper alloys indicates that the same type of hardening mechanism is probably present, although possibly some other interpretation might be placed upon the evidence. The curves show two facts very clearly. In the first place, no age-hardening takes place at 300° C. (570° F.) or below, while at 400° C. (750° F.) and above the aging is always accompanied by precipitation. In the second place, at any temperature at which aging takes place, the general forms of the parameter and hardness curves are unchanged and they bear the same mutual relation. The maximum hardness always occurs when about 20 per cent of the available copper has precipitated and the hardness rises rapidly before precipitation actually begins. As far as the importance of "knot" formation and precipitation is concerned, in relation to the hardening, these two factors are relatively unchanged by the temperature of aging; only the rate is temperature sensitive. The same mechanism, therefore, must be operative at all aging temperatures.

In this system, hardening by "knot" formation seems to be the most important factor. At 400° C. (750° F.), for instance, the hardness rises from 60 Rockwell B to 98 before precipitation begins, and this must be due to the rearrangement within the solid solution. When precipitation begins, the increase is only from 98 to 101 and then the alloy becomes softer. Similar curves are found at 500° C. (930° F.) and 600° C. (1110° F.), although the available methods of investigation are not entirely suitable for the more rapid changes. One might properly ask why the hardness maximum occurs after 20 per cent of the copper has been rejected, and whether this value has a particular significance. If

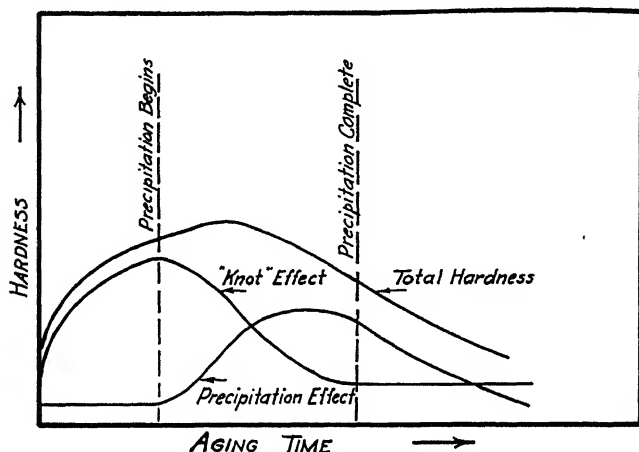


FIG. 4.—RELATION OF PRECIPITATION EFFECT AND "KNOT" EFFECT IN PRODUCING HARDNESS.

only a small amount of precipitate is needed to produce maximum hardness, it would seem that alloys of lower total copper content would give as high hardness values. The work of Smith and Palmer⁽¹⁾ shows clearly that this is not so. Apparently the best condition requires considerable copper still in solution, as well as a small amount in the form of copper crystals.

Theoretically, the hardness due to "knot" formation should be a maximum when precipitation just begins, should fall rapidly during the course of precipitation and become constant when the normal saturation value for that particular temperature is reached. The hardness due to the precipitate, however, should rise rapidly during the precipitation and reach its maximum at a point shortly before the completion of precipitation, the exact point depending upon the relative rates of precipitation and agglomeration of the precipitate. After the completion of precipitation a further softening would be expected as the result of increased agglomeration.

Fig. 4 shows how hardness curves due to these two factors can be combined to give a hardness curve similar to the experimental one.

Obviously, the actual shape and relative magnitudes of these curves are assumed, and it is further assumed that the two effects are additive. But the shape of the "knot-effect" curve is quite definite because, before precipitation, all of the hardening is due to this factor and the general appearance of the "precipitation-effect" curve is in line with accepted ideas, so that the situation presented here must represent many elements of the truth. At any rate, the shape of the observed hardness curve is not incompatible with a dual process of this type. It must also be clear that the position of maximum hardness is not necessarily of special significance and probably depends upon the rapidity with which knot hardening falls and precipitation-hardening rises, and upon the relative magnitudes of these two effects.

As a result of these experiments, there seems no reason to doubt the fact that in the age-hardening of iron-rich iron-copper alloys, the same type of mechanism is operative as has been found with duralumin. At all temperatures, however, precipitation plays rather a minor part in producing the maximum hardness. One might go so far as to predict that this same type of mechanism will be found in all alloys of the supersaturated solid solution type. Very few systems have been examined in sufficient detail to study this phase of the problem. In addition to duralumin, iron-carbon and iron-nitrogen have been examined by Burns⁽⁶⁾ who has shown that aging at room temperature causes the complete suppression of precipitation. Higher temperatures were not investigated. There is a great need for additional evidence along this line.

It is interesting to note that the iron-copper alloys of high purity show a complete lack of incubation period at all aging temperatures, while the corresponding copper steels of Smith and Palmer⁽¹⁾ showed such a delay plainly at the lower temperatures. It was also observed that the time required to obtain maximum hardness was considerably greater for the steels than for the pure alloy. Both of these facts indicate clearly that the atomic mobility is considerably reduced by the presence of the carbon and other constituents of the steel and emphasize the importance of this factor in aging phenomena.

The fact that throughout the progress of aging the diffraction lines remained consistently sharp, with a clear resolution of the chromium doublet, is of considerable importance. In the first place, this fact must indicate a remarkably uniform precipitation throughout the sample, for the photograms each represent a number of different grains. Even a small difference in copper content from grain to grain would cause a noticeable blurring. Furthermore, the fact of pronounced increase in hardness without precipitation and continued sharpness of the lines must mean that the lattice distortion that produces the hardening is of a special type. This same alloy hardened by cold work shows diffuse lines. For duralumin the diffraction lines remain sharp while hardening due to

knot formation but become diffuse as precipitation proceeds. It will be interesting to see whether this type of lattice distortion, which does not cause an increase in line breadth, will prove a common feature of age-hardening.

SUMMARY

1. The solid solubility of copper in iron has been redetermined using X-ray methods, and the maximum solubility has been set at 1.4 per cent copper by weight. The solubility decreases with decreasing temperature and is constant below 650° C. (1200° F.) at a value of 0.35 per cent.

2. Lattice changes during age-hardening have been correlated with hardness values and it is shown that the principal increase in hardness takes place prior to the precipitation of the copper-rich phase.

3. At all temperatures at which hardening takes place, the maximum hardness occurs when about 20 per cent of the available copper has been precipitated.

4. At all temperatures at which age-hardening can be observed, complete precipitation finally occurs accompanied by a decrease in hardness.

5. It is concluded that the age-hardening is due to two factors; the pre-precipitation rearrangement of the solid solution, which is the principal cause, and actual precipitation, which is the secondary cause. The relative magnitude of these two factors is not dependent upon the aging temperature.

ACKNOWLEDGMENT

The writer wishes to express his appreciation of the assistance rendered by Mr. A. R. Crawford, Mr. M. Cohen and Mr. T. E. Graves, who were associated with him in various portions of the work.

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1. Smith and Palmer: *Trans. A.I.M.E.* (1933) **105**, 133.
2. Buchholtz and Köster: *Stahl und Eisen* (1930) **50**, 687.
3. Webster, Christie and Pratt: *Trans. A.I.M.E.* (1933) **104**, 166.
4. Phillips and Brick: *A.I.M.E. Tech. Pub.* 563 (1934).
5. Merica: *Trans. A.I.M.E.* (1932) **99**, 13.
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DISCUSSION

(C. H. Herty, Jr., presiding)

C. S. SMITH,* Waterbury, Conn. (written discussion).—During the study of copper steels carried out by Palmer and myself two years ago, reasons were found to suspect that the alpha boundary in the copper-iron system, as determined by Buchholtz and Koster, was somewhat in error. The suspicion is confirmed by this work of Professor

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Norton. His careful re-determination of the boundary is a valuable contribution to our knowledge of this interesting system, and is of considerable practical importance in the rapidly developing field of copper-bearing ferrous materials.

As regards the correlation of lattice changes with hardness changes during the aging process, a factor of some importance in the interpretation of the data seems not to have been considered. Professor Norton finds the eutectoid transformation temperature, as shown by heating curves, to be between 855° and 860° C. The alloy used for the aging experiments contained 2.06 per cent copper, and was quenched from 860° C. This copper content is considerably greater than the alpha solubility (1.4 per cent) at this temperature, therefore it appears that the specimens contained some gamma (about 40 per cent), with a copper content of possibly 3 to 4 per cent, as well as saturated alpha. On quenching, the saturated alpha could be retained unchanged, but it is well established that the gamma changes over to alpha, and in this process an unknown amount of copper is precipitated.

At first sight this seems to throw some doubt on Professor Norton's determination of the alpha solubility at the highest temperature, since the maximum parameter obtained corresponds not to the solubility limit of equilibrium alpha but to the maximum amount of copper retained in alpha formed from gamma containing a higher percentage of copper. Buchholtz and Koster report lattice parameters that indicate that large amounts of copper may be held in this quenched alpha, but my work on hardness, as well as the author's X-ray determinations on quenched alloys, seems to indicate that the alpha formed by transformation of gamma loses just enough copper to make it equal in composition to saturated alpha at the eutectoid temperature. It is rather strange that this should be so, but because of it the determination of the solubility curve described in the paper is quite unaffected by the presence of gamma at the time of quenching.

In the interpretation of the aging experiments, however, account must be taken of the copper thrown out as the gamma changes to alpha. It seems probable that this copper is dispersed in a manner comparable with the very early stages of precipitation-hardening. Support for this view may be found in the fact that hypereutectoid copper-iron alloys quenched from above the eutectoid temperature show a hardness that increases with the quenching temperature until a value is reached that is not increased by subsequent precipitation treatment¹.

The absence of an incubation period in Professor Norton's experiments may well be due to the presence of nuclei arising from this gamma-alpha transformation, and the same factor may account for the more rapid aging observed as compared with low-carbon steels. So, too, it would seem that in computing the percentages of copper "precipitated" at various hardnesses, the total copper content of the alloy, rather than the maximum alpha solubility, should have been used. On this basis it appears that at the point of maximum hardness some 50 per cent of the available copper has been "precipitated," rather than 20 to 25 per cent. If this is the case, it is apparent that actual precipitation (used in Professor Norton's sense of change in lattice dimensions) is an important factor in the hardening of the alloys. It seems very probable that there is a wide variation in size of particles at any stage of the precipitation process, and the condition of maximum hardness occurring at 100 per cent precipitation could arise only from *all* particles reaching the critical size together—an extremely unlikely possibility.

With these considerations in mind, the question of the relative importance of "knot effect" and "precipitation" in the hardening of copper-iron alloys is still open. It is hoped that Professor Norton will be able to repeat his experiments on an alloy containing less copper than the maximum alpha solubility, quenched from the homo-

¹ Smith and Palmer: *Trans. A.I.M.E.* (1933) 105, 133 (Fig. 13).

geneous alpha field. Such results, coupled with those already obtained, would permit very valuable conclusions to be drawn regarding the mechanism of precipitation-hardening in this system.

J. T. NORTON (written discussion).—The criticism of Dr. Smith in the choice of composition and solution temperature during the aging experiments is entirely justified. It is felt that the results on the alpha-phase boundary are substantially correct but that rate of aging may be somewhat in error. Further work is now under way on new alloys and the X-ray and hardness results are supplemented by measurements of electrical resistance and dilation with the hope that the idea of "knot" formation in this system may be more completely examined.

Magnetic Aging of Iron Due to Oxygen

By T. D. YENSEN* AND N. A. ZIEGLER,† MEMBERS A.I.M.E.

(New York Meeting, February, 1935)

AGING is a term that connotes a slow change in properties under ordinary operating conditions. It can be accelerated by increasing the temperature and by mechanical straining. The magnetic properties of iron and some of its alloys have for many years been known to be subject to such a change. But the cause of the change was not recognized until a few years ago after mechanical age-hardening in non-ferrous alloys of the "duralumin" type had been definitely shown, by means of solid solubility curves, changes in electrical resistance and microanalysis, to be caused by slow precipitation of one or more constituents from the solid solution. The similarity between the solid solubility curves of such alloys (Fig. 1) and those for iron-nitrogen (Fig. 2) and iron-carbon alloys (Fig. 3) below the A_1 transformation point suggested at once that magnetic aging of iron might be caused by a similar process; namely, by the slow precipitation of carbon and nitrogen in the form of Fe_3N and Fe_3C at ordinary temperatures because of a cooling rate that had been too rapid to permit complete precipitation according to equilibrium conditions. This suggestion has since been amply confirmed, particularly by the comprehensive work of Köster¹ on the effect of nitrogen and carbon. Typical curves are shown in Fig. 4 for the relationship between aging temperature and coercive force.

Previous to the establishment of the precipitation-hardening theory it was thought that the effect of nonmetallic elements like C, N, O, etc., on the magnetic properties of iron was greatest when these elements were retained in solid solution, atomically dispersed throughout the interstitial spaces of the iron lattice².

Based on the theory that magnetic properties are intimately connected with the regularity of the lattice, it now follows quite logically that a greater effect on this regularity may be obtained when the above impurities are precipitated as very fine particles of Fe_3C , Fe_4N , FeO , etc., more or less uniformly dispersed within the grains. But if this is the case, it follows also that there must exist a relationship between the size

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¹ W. Köster: *Archiv. für das Eisenhüttenwesen* (1929) **2**, 8; (1930) **3**, 637; **4**, 289.

² T. D. Yensen: *Trans. Amer. Inst. Elec. Engrs.* (1924) **43**, 558.

of the particles and the magnetic properties just as Merica concluded that there is a relationship between the particle size of the precipitate and the mechanical properties³, as shown in Fig. 5.

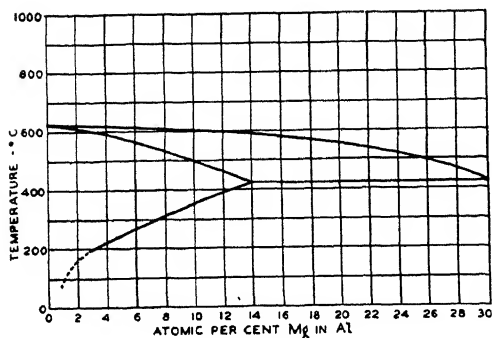


FIG. 1.

FIG. 1.—SOLID SOLUBILITY CURVE FOR MAGNESIUM IN ALUMINUM. [*Fink and Freche: Trans. A.I.M.E. (1934) 111.*]

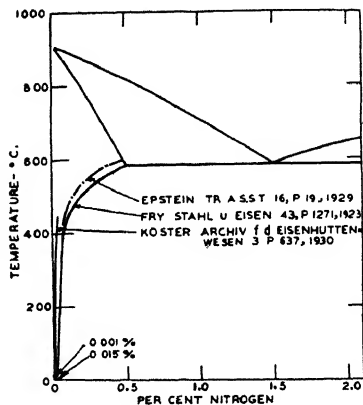


FIG. 2.

FIG. 2.—SOLID SOLUBILITY CURVE FOR NITROGEN IN ALPHA IRON.

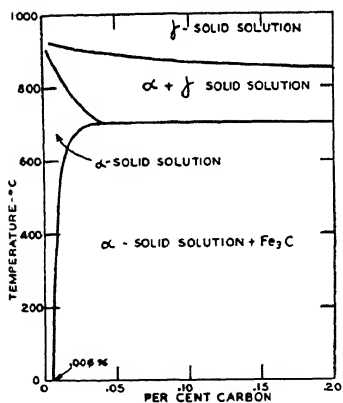


FIG. 3.

FIG. 3.—SOLID SOLUBILITY CURVE FOR CARBON IN ALPHA IRON. (*Köster.*)

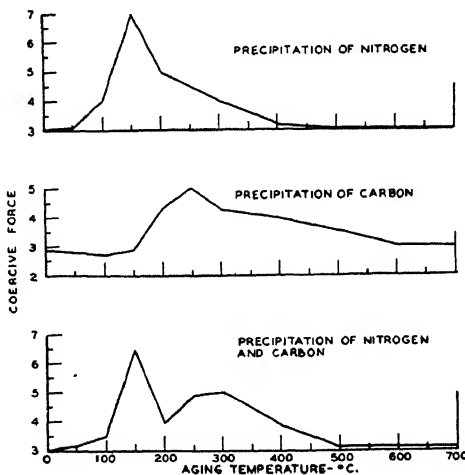


FIG. 4.

FIG. 4.—MAGNETIC AGING OF IRON DUE TO NITROGEN AND CARBON SEPARATELY AND COMBINED. (*Köster.*)

As the particle size undoubtedly increases with the annealing—or aging—temperature due to diffusion and coalescing the similarity between Köster's coercive force curves (Fig. 4) and Merica's hardness curves (Fig. 5) is no mere coincidence, and we may expect such a relationship

³ P. D. Merica: *Trans. A.I.M.E. (1932) 99, 13.*

to hold whenever we have similar conditions. As we believe that such conditions exist for oxygen and iron⁴ (Fig. 6), we should expect similar results in this case.

So far, however, the investigators who have worked on this subject have arrived at the conclusion that oxygen is not a cause of aging of iron. Thus, Burns⁵ describes certain results on the basis of which he expresses the opinion that oxygen cannot cause supersaturation in iron on rapid cooling, and consequently that no aging can be caused by oxide precipitation. His conclusions, however, are open to suspicion for the reason that apparently he did not use the kind of iron that he thought

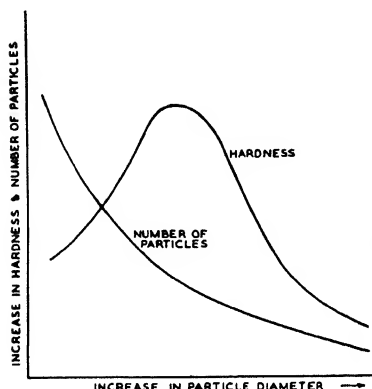


FIG. 5.

FIG. 5.—HARDNESS VS. PARTICLE SIZE.

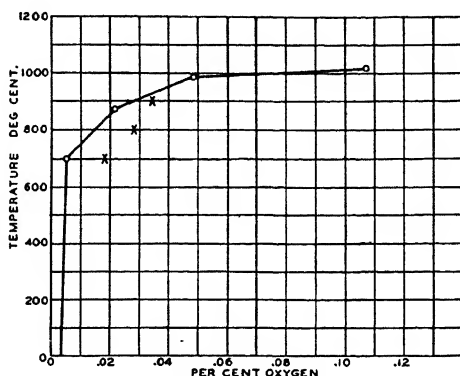


FIG. 6.

FIG. 6.—SOLUBILITY OF OXYGEN IN ALPHA IRON.

he did. He claims to have used Wemco iron obtained from Westinghouse Research Laboratories, but he gives an analysis that belies this claim. Wemco research iron (assuming that this is what he means), contains not over 0.01 per cent O_2 and at least 99.95 per cent Fe, while Burns states that his Wemco iron according to information accompanying it, contains 0.10 per cent O_2 and 99.85 per cent Fe. If Burns really had Wemco research iron, it would not be strange if he failed to detect any kind of supersaturation on quenching from the A_1 point, because the amounts of impurities are too low. If, on the other hand, he used 99.85 per cent iron, such as Armco iron, which actually contains about 0.08 per cent O_2 and 0.02 per cent C, it would be difficult to say whether his results might not be partly due to oxygen, as the relatively high carbon would tend to obscure the effect of other factors.

Eilender and his associates at Essen, on the basis of recent experiments⁶ have come to the conclusion that the solubility of oxygen in iron

⁴ N. A. Ziegler: Amer. Soc. Steel Treat. (1932) **20**, 73.

⁵ L. J. Burns: Classification of Alpha Iron-nitrogen and Alpha Iron-carbon as Age-hardening Alloys. *Trans. A.I.M.E.* (1934) **113**, 239.

⁶ *Stahl u. Eisen* (May 31, 1934) **54**, 554.

is very slight and does not depend upon the temperature. If this is true, these authors conclude that any change in coercive force and retentivity can only be assigned to strain elimination and coalescing of the insoluble FeO particles, or else to the small amounts of carbon and nitrogen present, and that no appreciable precipitation-hardening occurs in iron due to oxygen alone. It should be noted, however, that their samples either must contain considerably more oxygen or carbon than reported or else the effect of nitrogen and other factors must be so great as to mask all other effects, as the coercive force values are much greater than can be accounted for on the basis of the reported percentage of carbon and oxygen. From our own results⁷ the coercive force corresponding to 0.047 per cent O₂ should be about 0.065. As the authors report 0.72 oersteds for the sample containing 0.047 per cent O₂ + 0.007 per cent C + 0.006 per cent N₂, after annealing at 800° C. the effect of oxygen is less than 10 per cent of the total, so that even marked variations due to precipitation of oxygen could easily be overlooked. Furthermore, quenching in water from 930° C. (γ state) as in this instance, produces strains in the samples that greatly affect the magnetic properties. For these various reasons the statements by these authors cannot be accepted as conclusive evidence that oxygen does not produce precipitation-hardening. As the present authors have obtained results that contradict those of the authors mentioned above, they take this opportunity to present them here, making use of samples of even greater purity and of much better magnetic properties than those of the German authors.

Three ring samples were prepared from electrolytic iron melted under a blanket of hydrogen in a high-frequency induction furnace. The machined rings were first annealed for several hours in a stream of hydrogen at about 1400° C. to reduce the carbon, oxygen and sulfur contents to low values. During the cooling cycle they were further annealed at 850° C. for 10 hr. and then slowly cooled to produce large, unstrained grains. The rings were then tested magnetically. Using hysteresis loss (ergs per cu. cm. per cycle for $B = 10,000$) and maximum permeability as criteria, the results, together with the approximate chemical composition, are given in Table 1.

Carbon is present in amounts (0.0015 per cent) less than the generally accepted saturation value at room temperature (0.006 to 0.008 per cent)⁸, so that no complication should be caused by the most important incidental impurity. As nitrogen is less than 0.001 per cent and

⁷ T. D. Yensen and N. A. Ziegler: *Trans. Amer. Soc. for Metals* (1935).

⁸ This value was first published by the senior author in 1924 (reference of footnote 2) and has since been confirmed by Yap thermodynamically and by Bates [*Trans. Amer. Soc. Steel Treat.* (1932) 19, 449] experimentally. The present authors, however, now believe that the true solubility may be less than 0.006 per cent.

sulfur is of the order of 0.001 per cent⁹, we may safely assume that any effect that we obtain will be due to oxygen and to strains set up in the samples by rapid cooling.

TABLE 1.—*Ring Samples Annealed at 1400° C. in Hydrogen*

| Sample No. | Approximate Chemical Composition, Per Cent ^a | | | | | Magnetic Properties | |
|------------|---|----------------|----------------|----------------|-------|---------------------|-------------------|
| | C | O ₂ | H ₂ | N ₂ | S | W ₁₀ | μ _{max.} |
| AQ-1F | 0.0015 | 0.015 | 0.0005 | 0 | 0.001 | 171 | 63,300 |
| AQ-1G | 0.0015 | 0.015 | 0.0005 | 0 | 0.001 | 167 | 71,700 |
| AQ-1H | 0.0015 | 0.015 | 0.0005 | 0 | 0.001 | 160 | 71,400 |

^a From analysis of numerous samples similarly prepared and treated.

In order to introduce more oxygen into the samples than they originally contained they were heated in air for one hour at 900°, 800° and 700° C., respectively, and air-quenched. On the basis of Fig. 6, we should, if time were sufficient, expect oxygen contents of 0.03, 0.015 and 0.015 per cent, respectively (the latter because the samples already contained about 0.015 per cent to begin with). The actual oxygen contents, as obtained by analysis after completion of the aging investigation, were 0.035, 0.029 and 0.019 per cent, respectively (Table 4), and are shown by crosses in Fig. 6¹⁰.

TABLE 2.—*Rings Heated in Air for One Hour and Air-quenched*

| Sample No. | Temperature, Deg. C. | Expected Percentage of O ^a | Magnetic Properties | |
|------------|----------------------|---------------------------------------|---------------------|-------------------|
| | | | W ₁₀ | μ _{max.} |
| AQ-1F | 900 | 0.030 | 238 | 40,500 |
| AQ-1G | 800 | 0.015 | 182 | 64,000 |
| AQ-1H | 700 | 0.015 ^b | 161 | 66,000 |

^a See Fig. 6.

^b Solubility at 700° from Fig. 6 is 0.005 per cent, but oxygen content of sample is 0.015 to start with.

The magnetic properties after the air quench are given in Table 2. While the change in the samples heated at and quenched from 700° and 800° is comparatively slight (about 1 and 10 per cent respectively) the change in the one treated at 900° C. is considerable (nearly 40 per

⁹ H. Hanemann and A. Schildkötter [*Archiv für das Eisenhüttenwesen* (1929) **3**, 427] believe that the solubility of sulfur at room temperature is greater than 0.001 per cent. No definite value is available.

¹⁰ The discrepancy, whether due to error in the previous investigation or in the present one, is of minor importance for the purpose at hand, but should be borne in mind in connection with future work on solubility of oxygen in α iron.

cent). As the latter cannot be due solely to the higher oxygen content, as seen from the authors' previous results¹¹ (Fig. 7), it is probable that the air quenching has introduced much greater strains than in the samples quenched from 800° and 700° C. The latter particularly must be practically free from strains.

The air-quenched samples were next heated in vacuum for one hour successively at 200°, 400°, 600° and 800° C., followed in each case by

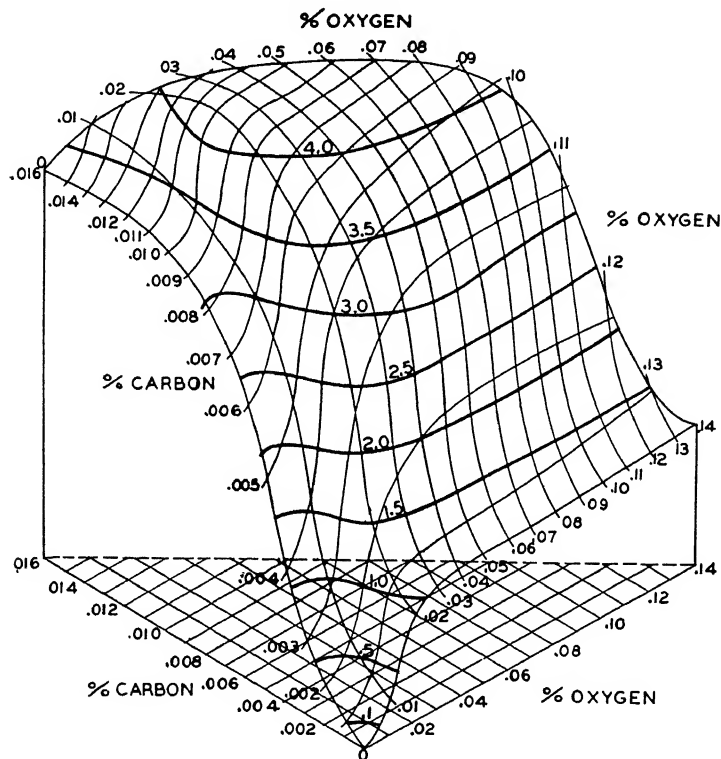


FIG. 7.—EFFECT OF CARBON AND OXYGEN ON MAGNETIC PROPERTIES OF IRON.

Numbers on surface are minimum reluctivity $\times 10^5$ (ρ min.). To get coercive force (oersteds) for $B = 10,000$ multiply numbers by 0.054. To get hysteresis loss (ergs per cubic centimeter per cycle) for $B = 10,000$ multiply numbers by 164.

slow cooling and magnetic testing. The results are shown in Table 3 and in Fig. 8. The actual values are shown connected by full lines. From this we find that for the 700° and 800° air-quenched samples these values correspond very closely to those obtained after the final 800° annealing. If we can assume that this would also be true for the 900° air-quenched sample cooled without introducing strains, the broken lines in Fig. 8 would result. We believe that this assumption is per-

¹¹ For 0.001 per cent C, an increase in oxygen from 0.015 to 0.035 per cent should increase the hysteresis loss by only 25 ergs, whereas the actual increase is 70 ergs. (T. D. Yensen and N. A. Ziegler: Reference of footnote 7.)

missible. With the above correction made for the 900° case, all the curves have the same general shape as those of Figs. 4 and 5, showing

TABLE 3.—*Rings Heated in Vacuum and Slowly Cooled*

| Sample No. | Temperature, Deg. C. | Magnetic Properties | | Temperature, Deg. C. | Magnetic Properties | | Temperature, Deg. C. | Magnetic Properties | | Temperature, Deg. C. | Magnetic Properties | |
|------------|----------------------|---------------------|---------------|----------------------|---------------------|---------------|----------------------|---------------------|---------------|----------------------|---------------------|---------------|
| | | W_{10} | $\mu_{\max.}$ | | W_{10} | $\mu_{\max.}$ | | W_{10} | $\mu_{\max.}$ | | W_{10} | $\mu_{\max.}$ |
| AQ-1F | 200 | 224 | 41,300 | 400 | 223 | 36,350 | 600 | 228 | 36,500 | 800 | 192 | 54,800 |
| AQ-1G | 200 | 187 | 57,000 | 400 | 220 | 51,700 | 600 | 212 | 49,000 | 800 | 183 | 67,500 |
| AQ-1H | 200 | 197 | 51,300 | 400 | 202 | 48,700 | 600 | 194 | 52,100 | 800 | 161 | 73,300 |

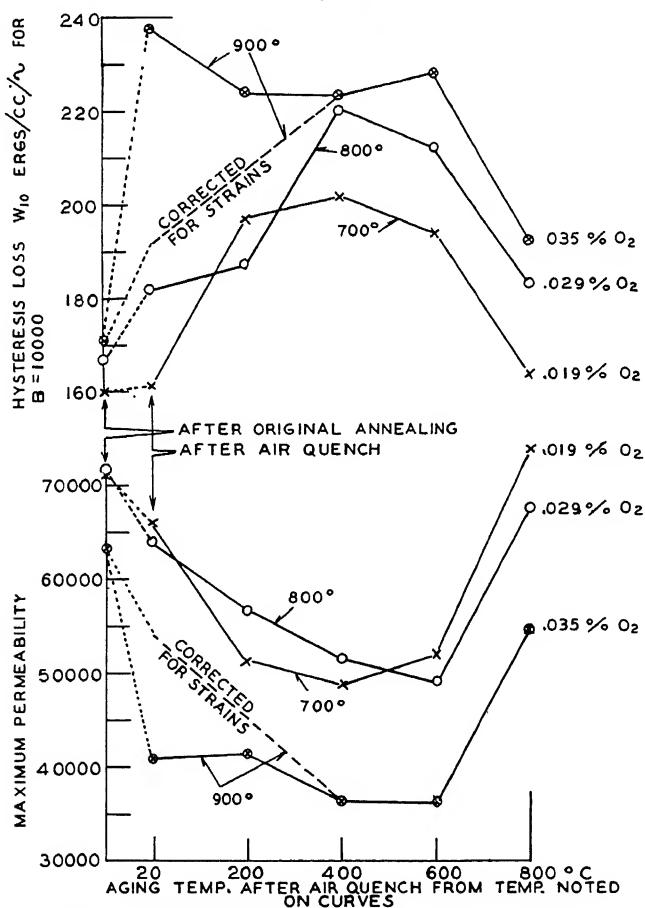


FIG. 8.—AGE-HARDENING OF IRON DUE TO OXYGEN.

that precipitation-aging or hardening occurs, due to oxygen, and that probably there is a certain critical particle size of the oxygen precipitate (probably FeO) that causes the greatest lattice deformation and thereby

has the greatest effect on the magnetic properties, similar in every respect to that of carbon and nitrogen. What this actual particle size is, the present investigation has not revealed except so far as to show that it is smaller than can be detected at a magnification of 500 diameters. Even after the 800° vacuum anneal no precipitates could be seen in any of the samples at that magnification, so that the critical particles may be of the order of 10^{-5} cm. dia.; i.e., almost colloidal.

TABLE 4.—*Chemical and Structural Characteristics after Final Heat Treatments*

| Sample No. | Percentages | | | | Grains per Square Millimeter |
|------------|-------------|----------------|----------------|----------------|------------------------------|
| | C | O ₂ | H ₂ | N ₂ | |
| AQ-1F | 0.0015 | 0.035 | 0.0006 | 0 | 0.16 |
| AQ-1G | 0.0015 | 0.029 | 0.0008 | 0 | 0.13 |
| AQ-1H | 0.0015 | 0.019 | 0.0005 | 0 | 0.14 |

It is interesting to note in conclusion that the magnetic properties after the final 800° treatment correspond fairly well to those predictable from Fig. 7 and the analysis given in Table 4, and that the solid solubility of oxygen at room temperature must be much below 0.019 per cent, but increasing with increasing temperature as shown in Fig. 6.

ACKNOWLEDGMENT

The authors wish to acknowledge the valued services of Miss Mildred Ferguson, Mr. S. L. Burgwin and Mr. Wilson Scott for the microanalysis, the magnetic testing and the heat treatments, respectively.

Use of Reflected Polarized Light in the Study of Inclusions in Metals

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(New York Meeting, October, 1934)

IN technological studies on steel considerable emphasis has been placed on the identification of the foreign inclusions, testimony of which is adequately given in the metallographic literature covering methods for their identification. The outstanding accomplishment in this field is the scheme devised by Campbell, Comstock and Wohrman for identifying various oxides, sulfides, silicates and other constituents by systematic etching tests and microscopic examination.¹ The time involved in carrying out this procedure has led to attempts to secure quicker methods, or at least to shorten the time required to secure essential information. An example of this is the use of dark field illumination,² but when this was tried out by the authors it was found that cavities and pits on the polished surface appeared bright on a dark field and could not be distinguished from small glassy inclusions.

Still another means is the Leitz Ultropak, an instrument equipped with optical units for the illumination of the specimen by reflected light to secure an effect similar to dark field illumination. The structures are made visible in exceedingly sharp details by utilizing the inherent properties of the samples, such as refractive index, absorption coefficients and reflection powers. We have had no experience with the Ultropak, but a recent paper by Benedicks and Löfquist³ describes methods for determining the refractive index of (Fe, Mn) O and MnS by the use of this equipment. Presumably this method would be subject to about the same limitations as dark field illumination, though the feature added by Benedicks and Löfquist appears to offer great promise in inclusion identification.

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¹ Method for Identification of Inclusions in Iron and Steel. National Metals Handbook, 1933 Ed., 636.

² This has been discussed recently by W. Zieler: Dark Field Illumination. *Metal Progress* (January, 1933).

³ C. Benedicks and H. Löfquist: On the Transparency of Sulphide and Oxide Inclusions in Steel. *Jernkontorets Ann.* (1933) 117, 443.

Other methods for identifying inclusions have been proposed, but they will be quickly passed over and we shall turn to quantitative determinations of the amounts present. Knowing the amounts of the various nonmetallics is obviously of great assistance in identifying the inclusions. While chemical extraction has been attempted, the first of these methods to attain prominence is the "vacuum fusion" method,⁴ which returns the "total oxygen." The most that this method gives is the amount of oxygen that occurs mainly as inclusions, but it does not define them more closely. A method that we have found to be much more useful is the electrolytic extraction of Fitterer,⁵ because it differentiates the kinds of inclusions and gives the amounts of each. Our experience with this method has been favorable, on the whole, though it does require more time than is desirable for many routine examinations.

The latest contribution to the quantitative estimation of the various oxides in iron and steel is the fractional oxygen method developed by Lewis Reeve,⁶ of this laboratory, which gives iron oxide, manganese oxide, silica and alumina separately. With the results of this method available, it becomes much simpler to identify inclusions and also to develop one's own technique of identifying them. After this has been done, the fractional oxygen determinations are useful, the more completely and positively to characterize the steel under investigation.

This brief review, although not complete, shows that two lines of thought have been followed in inclusion work: (1) analysis of the amounts present and (2) microscopic examination to identify them and to study their size, distribution, etc. To take full advantage of the information that can be obtained from the microscopic examination, one should also be able to make such distinctions as (1) that between iron oxide, the phase and iron oxide, a constituent of silicates or aluminates, and (2) that between glassy, optically active crystalline and opaque inclusions. It is in such work that the reflecting polarizing microscope makes a real contribution to the study of inclusions.

At the time the fractional vacuum fusion method was being developed various methods of checking its results were undertaken on similar samples. One was a microscopic examination upon average surfaces using a counting method upon the various inclusions to arrive at a percentage composition. Other check determinations were made by

⁴ See, for example, H. C. Vacher and L. Jordan: Determination of Oxygen and Nitrogen in Irons and Steels by the Vacuum-Fusion Method. *U. S. Bur. Stds Jnl. of Research* (1931) **7**, 375.

⁵ G. R. Fitterer: Method for Electrolytic Extraction of MnO, MnS, FeS, and SiO₂ Inclusions from Plain Carbon Steels. *Trans. A.I.M.E.* (1931) **95**, Iron and Steel Div., 196-218.

⁶ L. Reeve: Improvements in the Vacuum Fusion Method for Determination of Gases in Metals. *Trans. A.I.M.E.* (1934) **113**, 82.

electrolytic extraction followed by chemical analysis of the residue. Inasmuch as many of the samples analyzed were electric arc welds, the inclusions of which were very tiny, many of them escaped positive identification by the special etching tests commonly used to identify such inclusions microscopically.

During an examination of one of these welded specimens, about three years ago, a Leitz ore microscope fitted up for visual or photographic examination with reflected polarized light was used. When the specimen was examined with plane polarized light it appeared the same as when examined on the metallurgical microscope. When the analyzer prism was crossed with the polarizing prism, a positive and striking illumination was noted on all the transparent inclusions, whether large or small. This procedure has since been developed in our laboratory as a positive means for the routine examination and identification of inclusions. Reference was made to this work by one of the authors in oral discussions before this Institute at the February meetings of 1933 and 1934.

In attempting to learn what use has been made by others of reflected polarized light for the study of inclusions, many standard texts on mineralogy were consulted, but these deal entirely with rocks and minerals and but very briefly with reflection methods. An early observation that polarized light "illuminates" inclusions in metals seems to have attracted no attention and the only reference to this use of polarized light that we are aware of came out recently in a paper by Mauer and Brodman.⁷ These authors there refer to optically inactive and active inclusions as being oxides and silicates respectively. They state that glassy inclusions light up under crossed nicols and do not extinguish, and that they show normal red or green color with the gypsum plate. The transparent crystalline inclusions extinguish by reason of birefringence, and with the gypsum plate show colors of yellow to blue. They give an example in Figs. 7a and 7b in their paper, which show glassy inclusions that remain bright with crossed nicols.

POLARIZING MICROSCOPE FOR USE WITH REFLECTED LIGHT

The polarizing microscope as used with reflected light has been sufficiently described in the literature and need not be fully discussed here. Aside from noting that our instrument is the Leitz ore microscope, only a few of the more pertinent points will be covered. The polarizing microscope differs from an ordinary microscope chiefly in having a polarizing prism in the vertical illuminator for producing plane polarized light,

⁷ E. Mauer and L. Brodman: On Nonmetallic Inclusions in Steel. *Stahl u. Eisen* (1933) **53**, 319.

and an analyzer above the objective for "analyzing" the light that is reflected from the surface of the specimen.

A specimen illuminated by plane polarized light appears the same as if ordinary light were employed, but with the analyzer any effect that the specimen may have upon the original plane of vibration of the light can be rendered strikingly evident. The analyzer is rotatable and when in the "crossed" position, the planes of vibration of the two prisms are perpendicular to each other and the analyzer stops all the light that the polarizer normally transmits. This is true for the polished microsection, or the metallic portion thereof, and it appears dark with crossed nicols. When, however, an inclusion alters the plane of vibration of the incident illumination the analyzer permits that light to pass and the inclusion appears illuminated.

The analyzer can be withdrawn from the tube of the microscope, or, which amounts to the same thing, it can be rotated 90° in its mounting, to provide a rapid examination in polarized light with or without crossed nicols. The stage of the Leitz ore microscope may be rotated to orient specimens in different directions with reference to the planes of vibration of the nicols. For ordinary work the usual objectives without cover-glass correction may be used. The eyepieces should have cross-hairs to indicate the position of the planes of vibration of the two nicol prisms. The eyepiece is fixed in its proper position by means of a stud which fits in a notch in the draw tube.

The illumination for visual observation is supplied by a small 6-volt lamp enclosed in a lamp housing with a condensing lens and iris diaphragm. This is suspended from a bracket attached to the draw tube and focuses upon the polarizing prism in front of the vertical illuminator. Illumination for photographic work is provided by a mechanical feeding arc lamp with water-cooling cell, condensing lens and iris diaphragm.

SAMPLE PREPARATION

The preparation of the sample for the study of inclusions is properly regarded as of great importance to the success of the examination, though for our work with polarized light we use the same technique as that employed for ordinary illumination and examination with the metalurgical microscope.

The preliminary polishing steps are those usually employed, such as coarse grinding and fine grinding on the metallographic papers Nos. 1, 0, 00 and 000. The final polishing operation is carried out on an automatic polisher of the type designed by the Bureau of Standards⁸ and manufactured by the American Instrument Co., and we wish to

⁸ S. Epstein and J. P. Buckley: U. S. Bur. Stds. *Jnl. of Research* (1929) **3**, No. 117.

mention particularly the convenience and excellence with which it performs this important function. The specimen is mounted in a brass polishing cup with a special hard wax, Halowax No. 1014, which furnishes efficient lubrication through the preliminary grinding operations. The final polishing with the automatic machine is done on broadcloth-covered wheels using levigated alumina, which is automatically fed on the rotating disk from an air-agitated reservoir above the machine. Fig. 1 shows the V-pipe leading from the top of the flask to a vacuum line. A bottle is provided to prevent liquid from being carried over into the vacuum line. Air is drawn through the rubber hose and into the U-shaped glass tube connected to the V-shaped bottom of the reservoir. In order to escape, this air must pass through the liquid in the flask and out the exit at the top. The delivery tube to the polishing disk is at the side about 1 in. above the side U-tube and the flow of liquid is regulated by a glass stopcock. The delivery tube drops the abrasive at the center of the polishing disk. By this method we are able to set up the machine for polishing, regulate the flow of levigated alumina, and go about other duties until the polishing is completed. The automatic machine does an excellent job of polishing and with the automatic feeding device it becomes a practical tool for the metallographic laboratory.

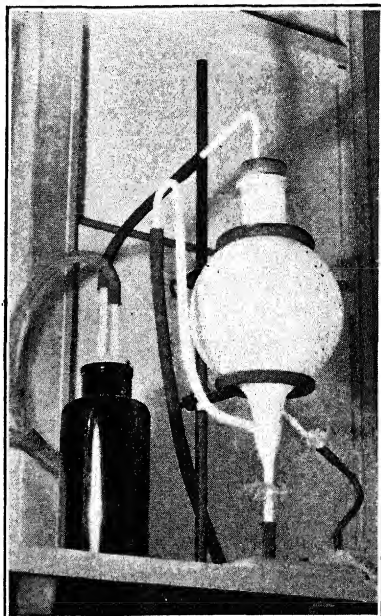


FIG. 1.—AIR-AGITATED RESERVOIR FOR THE LEVIGATED ALUMINA.

EXAMINATION OF INCLUSIONS WITH REFLECTED POLARIZED LIGHT

The metallographic specimen is examined in the as-polished condition. The first examination is made without crossed nicols to study the microstructure as ordinarily observed with the metallurgical microscope. A particular field of inclusions is then observed with the nicols crossed, which simply requires rotating the analyzer prism 90° . The metallic surfaces of the specimen is always dark but the inclusions may be dark or light, depending upon their type but independent of their size.

In our work these are characterized broadly as opaque or dark inclusions, and transparent or bright inclusions. In the former group we have iron oxide, manganese oxide, iron sulfide, manganese sulfide, chromium

oxide, titanium oxide, titanium nitride and zirconium nitride. After the inclusion has been classified as opaque it can be further identified by its color or etching tests or indirectly by fractional vacuum fusion or other means. It is not advisable to etch the specimen before examination in polarized light as this tends to attack and roughen the surfaces of the inclusions and sometimes attacks the matrix surrounding the inclusion to lend a certain "transparency" to the inclusion so attacked and make its identification less positive.

Inclusions of the second or transparent type can be more closely distinguished by means of their coloring and optical effects. As a simple case we may take the clear glass type of globular inclusions in weld metal and cast steel, which show a dark optical cross with concentric rings. A typical example of this is shown by Figs. 2 and 3, of a globular

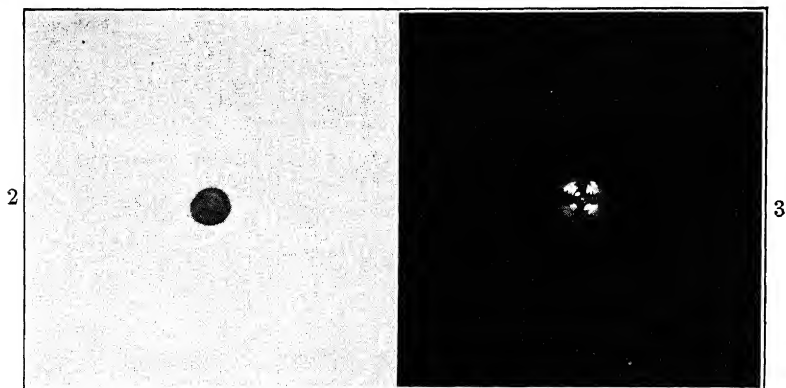


FIG. 2.—CLEAR GLASS TYPE OF GLOBULAR SILICATE INCLUSION WITH ORDINARY LIGHT. $\times 1000$.

FIG. 3.—SAME INCLUSION AS FIG. 2 SHOWING THE TYPICAL DARK OPTICAL CROSS WITH CONCENTRIC RINGS, TAKEN WITH CROSSED NICOLS. $\times 1000$.

silicate inclusion in ordinary light and with crossed nicols. The pattern produced by crossed nicols is typical and is positive in identifying tiny globular inclusions of silicates. The optical cross remains in a fixed position, with respect to the cross-hairs in the eyepiece, when the inclusion is rotated on the stage. At times the transparent silicates may be slightly contaminated with metallic oxides that are miscible in the silicates, and this produces a coloration in polarized light with crossed nicols. We have observed such colors as pink, brown, green, and blue, which may be due to contamination by metallic oxides. Even though these colors occurred in globular silicate inclusions, the dark optical cross was still evident. Other contaminations of globular silicate inclusions tend to reduce the clear transparency to a milkiess. Observations of such inclusions show them to be bright with crossed nicols but lacking the dark optical cross. It is believed that calcium oxide or fluoride may be responsible in one particular case at least for this apparent milkiess.

We have observed silicate inclusions that originally were globular and showed the dark optical cross but which lost the optical cross when the specimen was forged into a pancake and the inclusions became flattened. Similarly, siliceous inclusions, such as stringers and streaks in rolled bars and plates, show up bright or colored but without the dark optical cross. These inclusions usually are contaminated with oxides, which lower the melting point and make them more plastic at the rolling or forging temperature, so that usually they appear in elongated shapes. As the amounts of these contaminating oxides increase, we run into iron and manganese silicates. The quantitative methods now in use cannot distinguish between FeO and MnO, which occur as separate phases or as duplex inclusions, and FeO and MnO which are in combination as silicates, but this distinction can be readily made by examination with reflected polarized light.

Finally, we have transparent, crystalline inclusions, which illuminate with crossed nicols but extinguish when the stage is rotated.

RESULTS OBTAINED IN TYPICAL CASES

Fig. 4 shows several large globular inclusions in a cast, heat-resisting alloy with 29 per cent chromium and 11 per cent nickel, taken with ordinary illumination. Many of these appear glassy and would be readily recognized as silicates. There are three cavities in this photograph, a small globular cavity at the upper left-hand corner, one near the center and one at the bottom and center. This photograph was made on a regular metallurgical microscope, on which the image is reversed as compared to the polarizing microscope.

Fig. 5 is the same field as Fig. 4, except that the image is reversed, and shows the inclusions as seen with crossed nicols. All the silicate inclusions are bright and all show the dark optical cross, though the photograph does not show this clearly in every case. It is difficult to photograph large and small globular silicates and record the dark optical cross in each individual inclusion as we have shown in Fig. 3. The intensity of the light coming from the inclusions varies, which would require a different exposure time for each size of globule. The normal exposure time for making the photographic negatives with crossed nicols was about 20 to 25 minutes, using Wratten and Wainwright metallo-graphic dry plates with a K-2 yellow filter and a carbon arc lamp with 4.5-mm. horizontal carbon and 6-mm. vertical carbon. When the visual observations are made, usually with the 6-volt lamp, the dark optical cross is clearly discerned. It will be noted that none of the three globular cavities are bright. Therefore this method easily distinguishes voids from real inclusions. All the inclusions except the three on the left-hand side of the photograph in ordinary illumination, Fig. 4, are shown as bright with crossed nicols. Upon visual examination these were

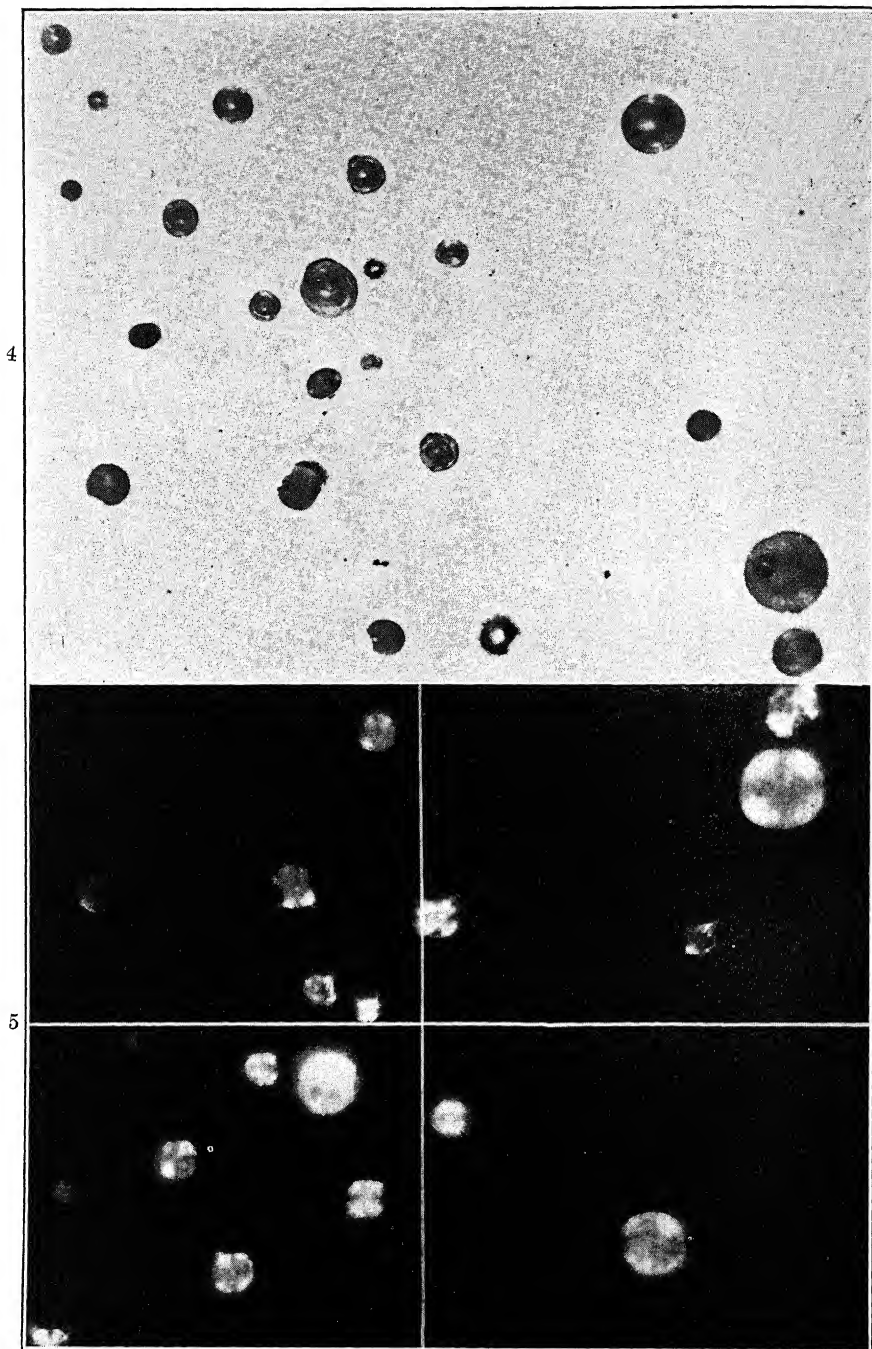


FIG. 4.—LARGE GLOBULAR INCLUSIONS IN CAST HEAT-RESISTING ALLOY, TAKEN WITH ORDINARY ILLUMINATION. $\times 350$.

FIG. 5.—SAME FIELD AS FIG. 4, EXCEPT THAT IMAGE IS REVERSED, TAKEN WITH CROSSED NICOLS. $\times 350$.

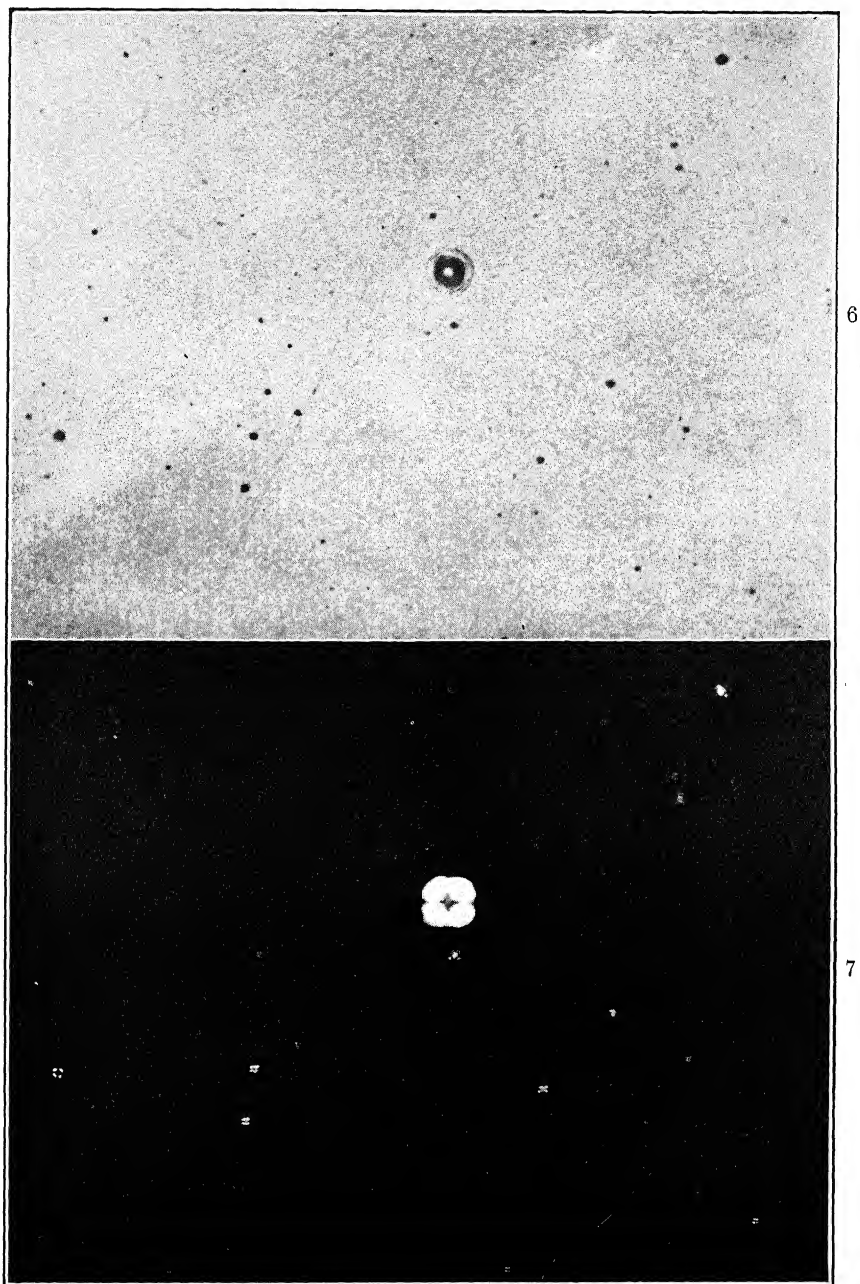


FIG. 6.—GROUP OF TINY GLASSY SILICATE INCLUSIONS IN WELD METAL MADE WITH CELLULOSE-COATED ELECTRODES. $\times 430$.

FIG. 7.—SAME FIELD OF INCLUSIONS AS FIG. 6 TAKEN WITH CROSSED NICOLS. SHOWING "STARRY-NIGHT" EFFECT. $\times 430$.

observed as opaque inclusions, and it is interesting to note that they appear somewhat like the real silicates with ordinary illumination. When viewed visually, the eye is sensitive enough to discern a slight difference between metal and opaque inclusions and this may be intensified photographically.

Fig. 6 shows a characteristic patch of tiny inclusions in weld metal made with cellulose-coated electrodes. This is the type of fine inclusions which we referred to as being difficult to identify by ordinary etching technique. Many tiny inclusions appear in Fig. 6 taken with ordinary illumination, and, except for the large inclusion in the center, none appear to be glassy. Fig. 6 was taken on the polarizing microscope.

Fig. 7 shows the beautiful effect upon the same field of inclusions when crossed nicols are used. We have termed this the "starry-night" effect. A close study of this figure reveals almost 100 per cent of the inclusions as silicates. Those appearing on the top half of Fig. 6 did not record on our photographic negative largely because the exposure time of 35 min. was not long enough. However, our visual examination of this field showed all of the inclusions present to be silicate inclusions. The dark optical crosses are shown nicely in Fig. 7 for most of the silicates. Similar welds of the type shown by Figs. 6 and 7 have been analyzed by the fractional oxygen method and found to contain about 0.01 per cent or less oxygen as MnO. An FeO fraction is not present. The amount of oxygen as SiO₂ ranged from 0.05 to 0.075 per cent and the amount of oxygen as Al₂O₃ from about 0.002 to 0.008 per cent. This confirms the findings with reflected polarized light.

Fig. 8 shows a specimen of weld metal made with the heavily coated slag-type of electrodes. The metal structure shows many tiny single-phase inclusions, some light and some dark in color, and these appear to be the same constituents that compose the larger duplex inclusions. A large globular inclusion is shown, which is not at all glassy and appears to be complex with ordinary illumination.

Fig. 9, of the same field taken with crossed nicols, shows none of the small inclusions and it is only the large inclusion that lights up as a milky silicate contaminated by metallic oxides. The duplex inclusions are opaque and were identified as FeO and MnO by etching tests, which agrees with the findings of fractional vacuum fusion analysis. Likewise the finely disseminated inclusions are either FeO (light) or MnO (dark).

Other welds of the type shown by Figs. 8 and 9 have been analyzed by the fractional oxygen method and found to contain a high FeO content with about 0.20 per cent oxygen as FeO and a small MnO content. The amount of oxygen as SiO₂ is about 0.03 per cent and as Al₂O₃ about 0.02 per cent.

Fig. 10 shows a specimen of weld metal with a different type of slag-coated electrode. Two inclusions of similar size are shown. The

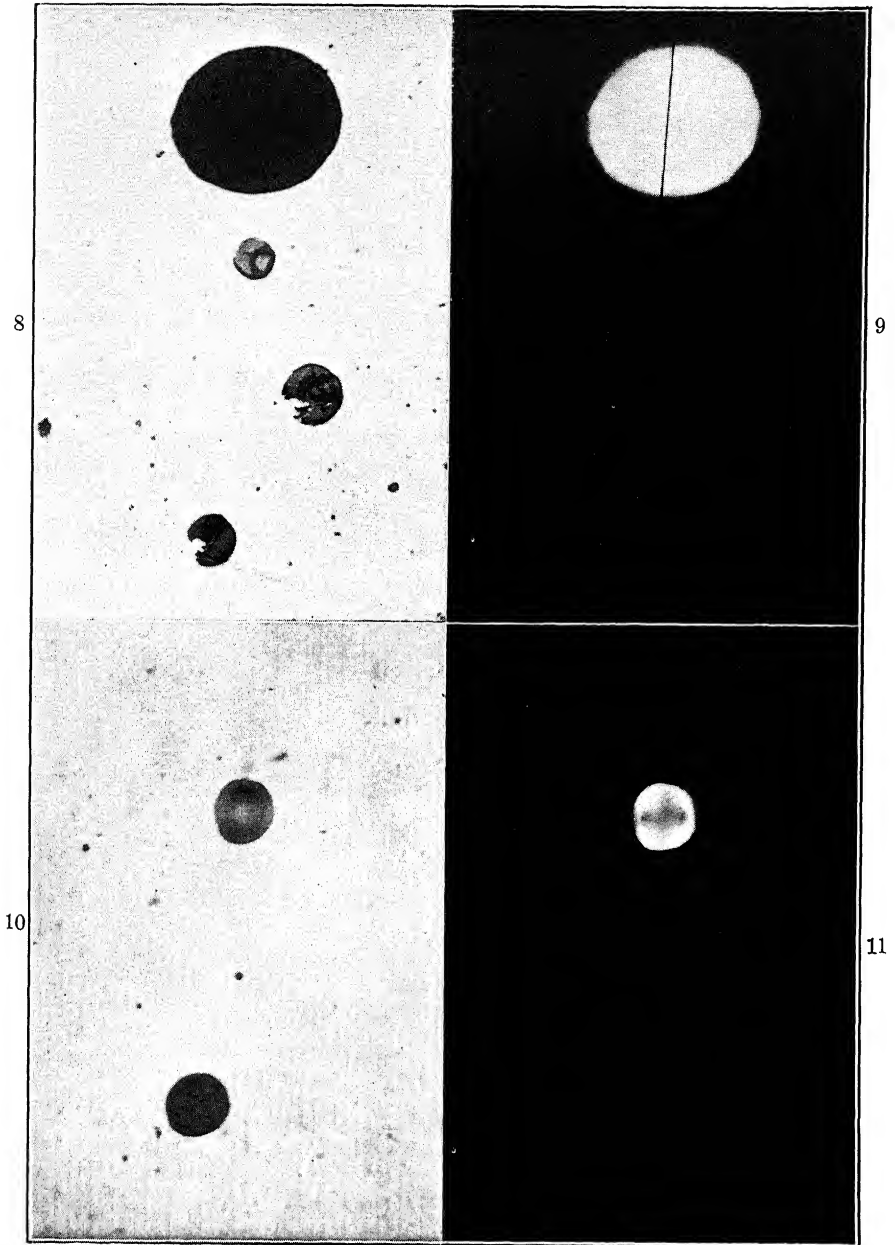


FIG. 8.—INCLUSIONS IN WELD METAL MADE WITH HEAVILY COATED SLAG-TYPE OF ELECTRODES, TAKEN WITH ORDINARY ILLUMINATION. $\times 500$.

FIG. 9.—SAME FIELD OF INCLUSIONS AS FIG. 8 SHOWING APPEARANCE OF OXIDES (NOT SHOWN IN DARK BACKGROUND) AND MILKY COMPLEX SILICATES WITH CROSSED NICOLS. $\times 500$.

FIG. 10.—INCLUSIONS IN WELD METAL MADE WITH DIFFERENT TYPE OF SLAG-COATED ELECTRODE FROM THAT SHOWN BY FIG. 8. $\times 1000$.

FIG. 11.—APPEARANCE OF SAME INCLUSIONS AS IN FIG. 10 WITH CROSSED NICOLS. $\times 1000$.

upper inclusion is glassy in appearance while the lower inclusion is darker and duplex. It appears somewhat similar to the large inclusion shown in Fig. 8.

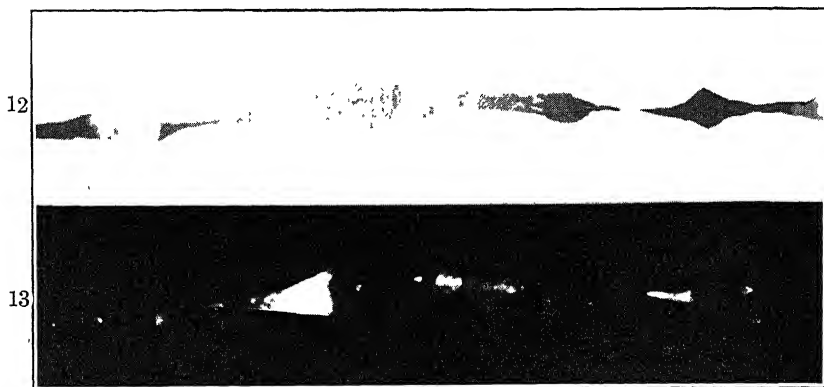


FIG. 12.—STRINGER INCLUSION FOUND IN SEMI-RIMMING STEEL. $\times 300$.

FIG. 13.—SAME FIELD AS FIG. 12 WITH CROSSED NICOLS. $\times 300$.

Fig. 11, taken with crossed nicols, shows only the upper inclusion to be bright. The dark optical cross is observed. The lower inclusion was faintly translucent when the light to the vertical illuminator was stopped down to a pinhole. When this is done, the field becomes very

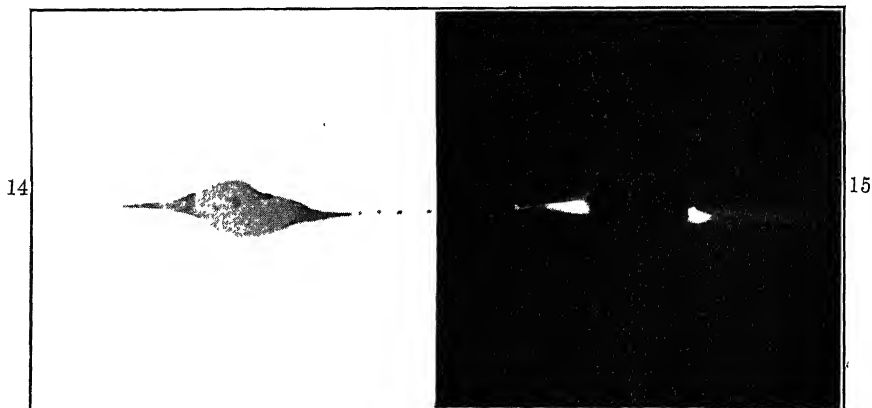


FIG. 14.—TYPICAL INCLUSION FOUND IN SEMI-RIMMING STEEL. $\times 500$.

FIG. 15.—SAME INCLUSION AS FIG. 14 SHOWING SILICEOUS TAILS, WITH CROSSED NICOLS. $\times 500$.

dark and slight translucency is noticed by careful visual examination. However, the silicate present was so much contaminated that its transparency was not sufficient to photograph with normal exposure. Fractional vacuum fusion analysis showed that this inclusion was undoubtedly contaminated with FeO and MnO.

Similar welds of the type shown by Figs. 10 and 11 were found to contain about 0.06 per cent oxygen as FeO and MnO, about 0.09 per cent oxygen as SiO₂, and about 0.01 per cent oxygen as Al₂O₃. This shows a lower content of FeO and MnO and a higher content of SiO₂ than the weld of Figs. 8 and 9, and again brings out the correlation with the microscopic examination with reflected polarized light.

Fig. 12 is a photograph of a stringer inclusion found in semi-rimming steel. This inclusion was found in 3½-in. thick plate rolled from a large ingot. Three distinct shades are noted in this stringer. The very light gray is an iron-rich oxide and the darker gray is a manganese-rich oxide. The darker oxides are probably contaminated with some manganese sulfide. The more plastic portions of the inclusion have a slightly mottled appearance, which is difficult to discern at the magnification of the photograph.

Fig. 13, of the same inclusion with crossed nicols, shows the plastic portions of the inclusion to be bright, and these are identified as silicates, probably with manganese contamination.

Fig. 14 is a photograph of a type of inclusion often found in semi-rimming steel. This inclusion was found in the same type of steel as that of Fig. 12. The photograph shows that the tails of the inclusion were more plastic at the rolling temperature employed than was the body of the inclusion. The pale color of the center of the inclusion suggests that it is an oxide and it reacted to etching tests as FeO and MnO with a slight contamination of MnS.

Fig. 15, of the same inclusion with crossed nicols, shows the tails to be bright and identifies them as silicate, probably manganese silicate. Similar specimens of this steel have been analyzed by the fractional oxygen method and found to contain about 0.010 per cent oxygen as FeO and MnO, about 0.010 per cent oxygen as SiO₂ and about 0.003 per cent oxygen as Al₂O₃.

Fig. 16 is a photograph of a low-carbon steel wire after severe cold drawing. The cold working has broken up most of the stringer inclusions shown. Most of the light gray stringers are identified as manganese sulfide and the larger dark inclusions as manganese silicates.

Fig. 17, of the same field with crossed nicols, shows the bright silicates. The largest light gray stringer shown in Fig. 16 below the silicate stringer near the top is observed to be bright with crossed nicols, while all the other light gray inclusions are opaque. This particular field was photographed to show that with ordinary illumination quite dissimilar inclusions may be similar in color and appearance. In this case all the light gray inclusions would be assumed to be manganese sulfide. With a rapid examination in reflected polarized light many of these light gray inclusions could be examined and positively identified as opaque manganese sulfide or transparent silicate.

Fig. 18 shows a photograph of a semi-rimming steel partially killed with aluminum. The specimen shown came from the top discard of the ingot

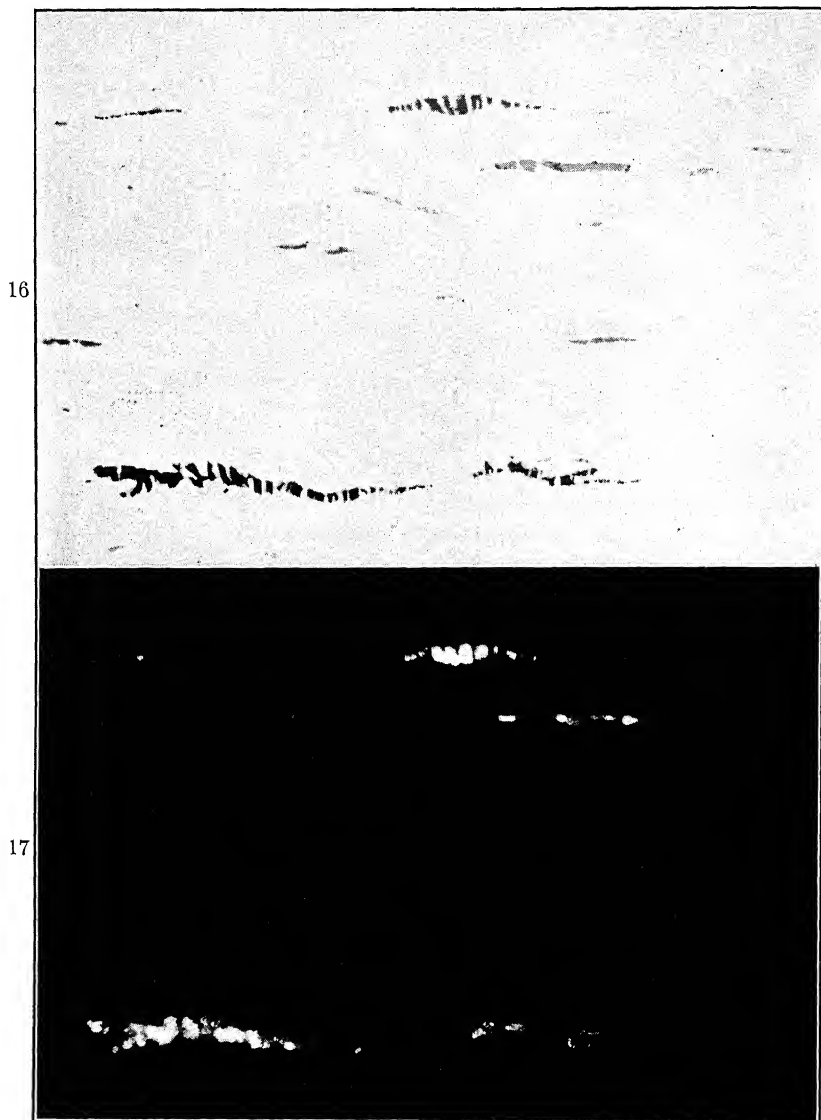


FIG. 16.—SULFIDE AND SILICATE INCLUSIONS IN COLD-DRAWN LOW-CARBON STEEL WIRE, TAKEN WITH ORDINARY ILLUMINATION. $\times 350$.

FIG. 17.—SAME FIELD OF INCLUSIONS AS FIG. 16 WITH CROSSED NICOLS. $\times 350$.

after rolling and shows the alumina segregation. The inclusions present have the typical appearance of alumina and are rather difficult to polish because of their brittle nature. This photograph was made on a regular metallurgical microscope, on which the image is reversed as compared to the polarizing microscope.

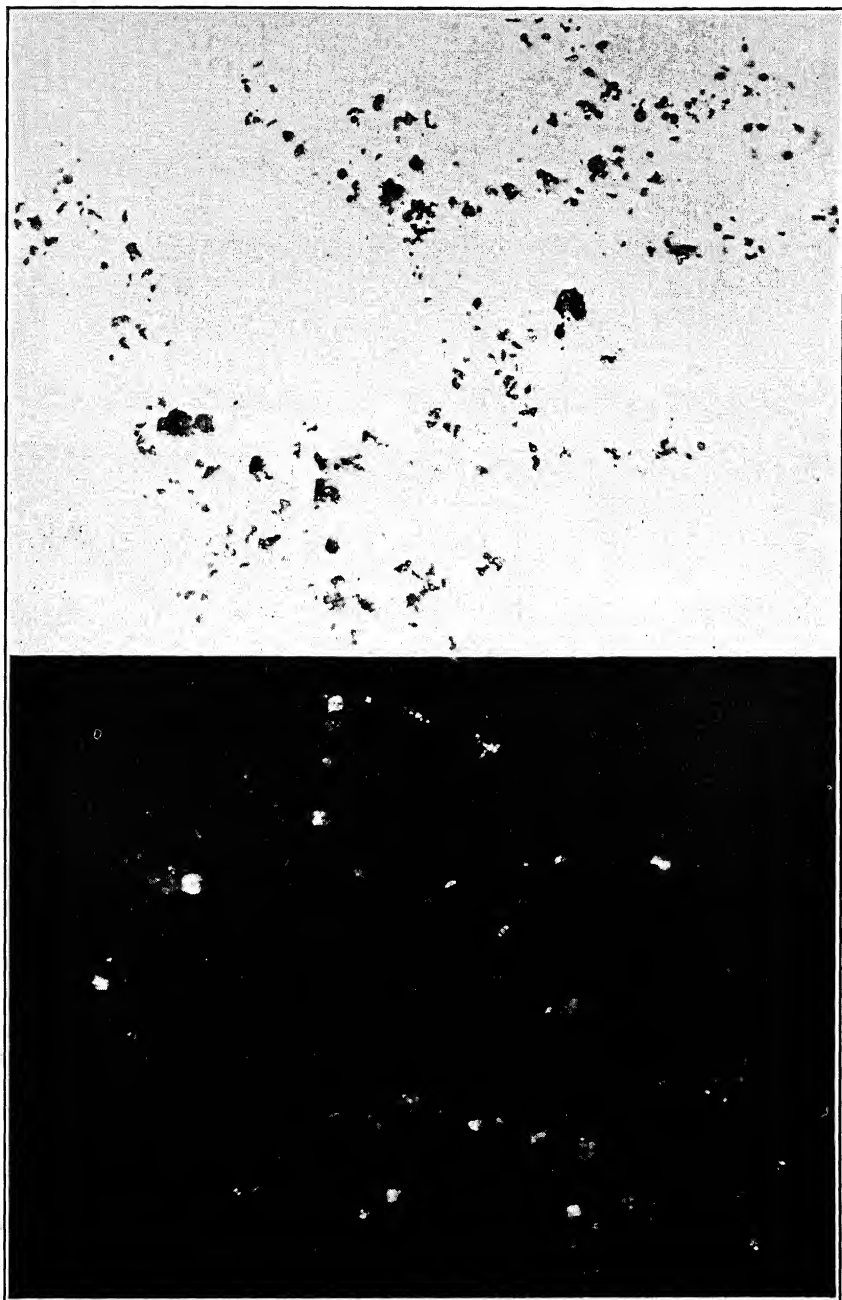


FIG. 18.—ALUMINA CLOUD IN TOP DISCARD OF ROLLED SEMI-RIMMING STEEL, PARTIALLY KILLED WITH ALUMINUM. $\times 350$.

FIG. 19.—SAME FIELD OF INCLUSIONS AS FIG. 18, EXCEPT THAT PHOTOGRAPH IS REVERSED, SHOWING OPTICALLY ACTIVE ALUMINA WITH CROSSED NICOLS. $\times 350$.

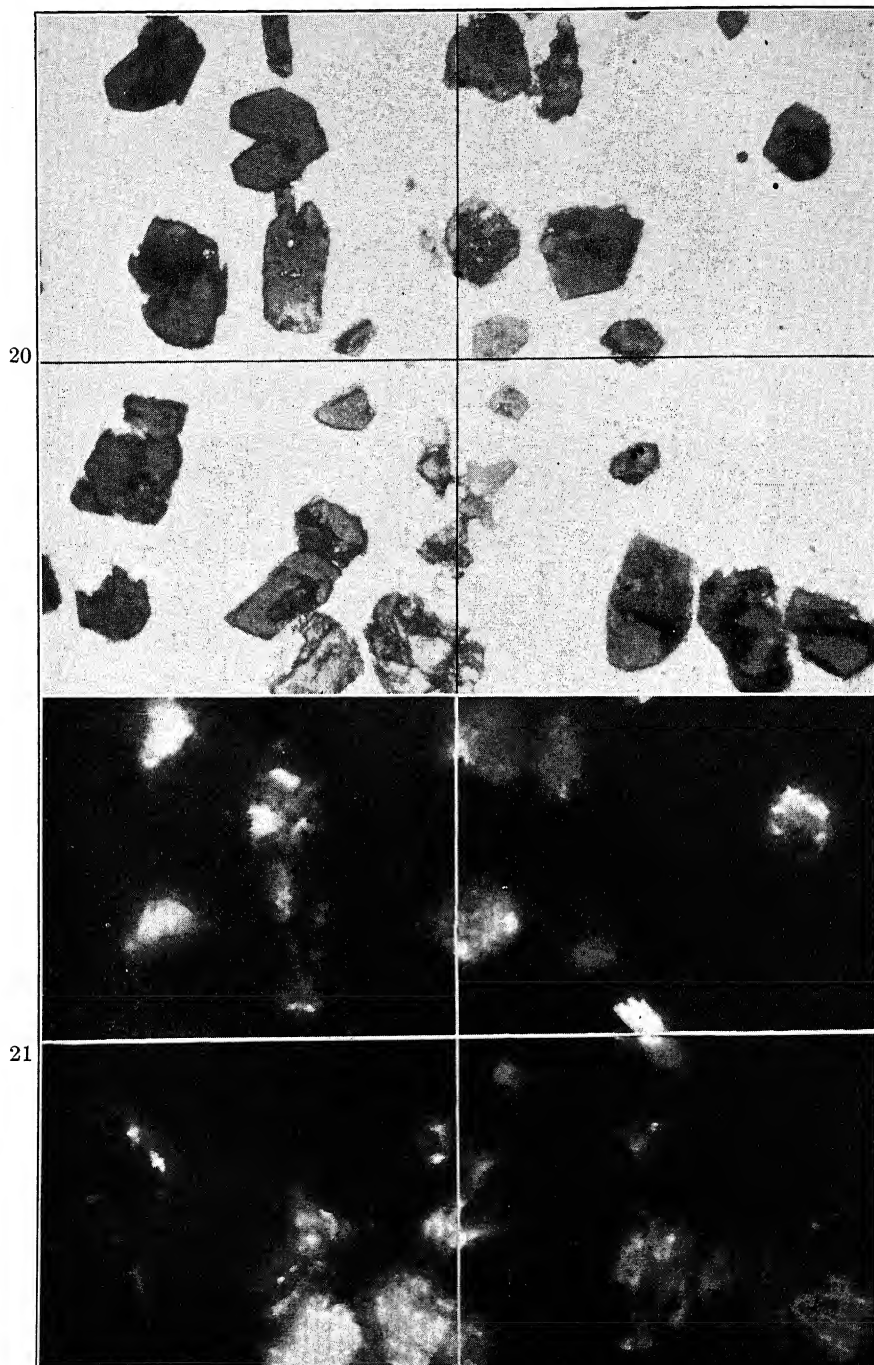


FIG. 20.—COMPLEX OXIDES FORMING CRYSTALLINE INCLUSIONS. $\times 500$.

FIG. 21.—SAME FIELD OF INCLUSIONS AS FIG. 20, SHOWING DOUBLE REFRACTION OF COMPLEX CRYSTALLINE INCLUSIONS WITH CROSSED NICOLS. $\times 500$.

Fig. 19, of the same field, except that the photograph is reversed, shows the alumina inclusions in polarized light with crossed nicols. Probably these inclusions contain small amounts of FeO as a compound of the spinel type (Hercynite $\text{FeO} \cdot \text{Al}_2\text{O}_3$). Herty gives the compound $\text{FeO} \cdot 2\text{Al}_2\text{O}_3$. The individual particles of alumina light up and do not extinguish or change in light intensity with rotation of the stage. A few globular silicates are observed among the alumina particles. The reflecting polarizing microscope does not distinguish between silicate and alumina except that the alumina particles never show the dark optical cross. Distinction between alumina and silicate is also based upon the appearance of the inclusions with ordinary illumination.

Fig. 20 is a photograph of a special Fe-Cr-Al alloy after heating to an elevated temperature. The cast alloy before heating was practically free from inclusions. During the heating, oxygen penetrated the surface of the alloy and combined in the solid state with constituents of the alloy to form a complex crystalline oxide. The inclusions are slate gray in ordinary illumination and are hard and brittle.

Fig. 21 is a photograph of the same field of inclusions in polarized light with crossed nicols. The crystalline inclusions show double refraction; that is, they light up and darken four times during a complete revolution of the specimen on the microscope stage. The photograph shows some of the inclusions dark and others bright. Optically anisotropic substances appear bright on a dark field in positions intermediate between those of extinction. With ordinary illumination a number of inclusions were observed to have a duplex structure; that is, smaller cubical crystals were contained within the large inclusions. These were slightly different in color and parts of the inclusions appeared glassy. When these same inclusions were examined in polarized light with crossed nicols, the colors red, green and yellow were observed.

The photographic negative of Fig. 21 was exposed a long time to show that some of the inclusions in Fig. 20 are dark. However, if the stage were rotated less than 90° from the position shown by the photograph in Fig. 21, the dark inclusions would be bright, and vice versa.

To illustrate how reflected polarized light may be used to identify foreign inclusions, the following is the story of an interesting shop problem that came to the Research Department. It relates to a bar of forging steel of chemical composition: C 0.21 per cent, Mn 0.62, Si 0.026, P 0.03, S 0.035, and with the usual microstructure. The steel bars were placed on the refractory hearth of a forging furnace and heated to a temperature of 2345° to 2380° F. in 45 min. After a shutdown for furnace repairs, it was noticed, when production began again, that the wear on the forging dies had increased considerably. A specimen was obtained from one of the bars heated to the forging temperature, but not forged, and the structure at the surface was found to show some inclusions in globular

shape and a slight decarburization of about 0.004 in. An examination of this specimen was made on the metallurgical microscope and the inclusions appeared to be similar except that some were lighter in color than others and none of the globular inclusions appeared to be glassy, like those shown in Fig. 4. Had we not examined this specimen with the polarizing microscope we might have identified the inclusions simply as oxides. However, the character of the inclusions with crossed nicols is shown in Fig. 22 at a magnification of 350. It is apparent that the inclusions on the outer surface are dark and that the inclusions below this are

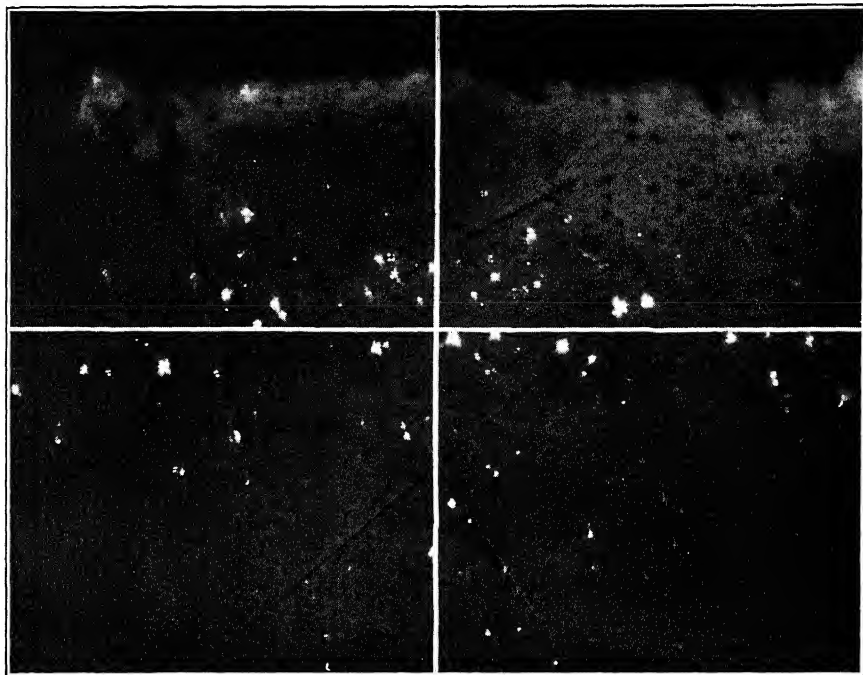


FIG. 22.—INCLUSIONS BELOW SURFACE OF BAR HEATED TO FORGING TEMPERATURES, SHOWING BRIGHT SILICATES WITH OPTICAL CROSS IN POLARIZED LIGHT WITH CROSSED NICOLS. NOTE DARK OXIDES UNDER SURFACE. $\times 350$.

transparent silicates. The dark optical crosses in many of the globular silicates are distinct and positively identify these inclusions as silicates and show that the bar was not mechanically worked after their formation. The photographic negative was exposed long enough to bring out the opaque oxides that appear mostly under the outer surface. A McQuaid-Ehn carburizing test for abnormality on the specimen of Fig. 22 showed abnormality at the surface, but this condition was confined to the layer containing the oxides. An examination with crossed nicols was made around the periphery of the forging bar, and we found the silicate inclusions on only one side of the bar, although the oxide penetration was quite uniform. A thorough examination of the cross-section of the bar was

made with crossed nicols, but, as is suggested by the chemical analysis of this material, we did not find any siliceous inclusions except those mentioned. After these observations were made it was quite apparent what caused the excessive wear on the forging dies. The scale on the heated bars had picked up silica, which caused it to be more adhesive to the surface of the forging bars and consequently caused the excessive wear of the dies. Upon tracing the source of the silica, it was found that a siliceous refractory had been used to repair the hearth of the forging furnace. We may also assume that forgings that had been treated in this way would show soft spots after heat treating.

SUMMARY AND CONCLUSIONS

The use of the reflecting polarizing microscope for the identification of optically active, glassy and crystalline inclusions has been described and a number of photomicrographs shown to illustrate the results.

A positive identification for the globular clear glass type of silicate inclusions showing the dark optical cross with concentric rings has been given, and shown to apply to both large and very tiny inclusions.

The effects of certain miscible metallic oxides when dissolved in silicate inclusions have been discussed.

The translucency or milkiness of other silicate inclusions has been discussed with reference to contamination by calcium oxide or fluoride.

The occurrence of elongated silicates in rolled or forged bars and plates has been illustrated by examples of commercial products.

The identification of alumina particles has been pointed out and the optical properties in reflected polarized light with crossed nicols discussed.

The optical behavior of an optically active and doubly refracting inclusion has been illustrated with a certain complex oxide which resulted from the diffusion of oxygen into an Fe-Cr-Al alloy.

In particular it has been shown how simple it is to distinguish between opaque and transparent inclusions and to show whether FeO occurs as a phase or in combination with SiO_2 or Al_2O_3 . It is also suggested that once the major distinctions have been made, more complete identification can then be made by subsequent tests.

The authors' purpose in this paper has been solely to describe a new metallurgical tool and to point out the gratifying results that have been obtained with it. They do not claim that this method will replace any quantitative methods now in practice but they would like to point out that there is a use for the reflecting polarizing microscope in the study of inclusions in metals.

ACKNOWLEDGMENTS

The authors wish to give due credit to Dr. Fritz Wienert, ore petrologist at the A. O. Smith Corporation, 1930-1932, and to Dr. H. Lange-

beck, research metallurgist, who were connected with the early part of this work, and they wish to express their thanks to the officials of the A. O. Smith Corporation for permission to publish the results.

DISCUSSION

(Francis B. Foley presiding)

J. CHIPMAN,* Ann Arbor Mich.—Mr. Urban and I have been doing some experiments on the identification of inclusions, and we have found the polarizing microscope exceedingly useful. Unfortunately, we only had a little ore microscope through which we could see the “starry night,” but we were unable to photograph it. However, our observations, in almost all respects, are in accordance with those that have been reported.

In one respect, we have found something different on the chrome inclusions, which in ordinary photomicrographs looked like those shown by the authors. Our chrome inclusions were entirely inactive optically. That is to say, they were isotropic instead of anisotropic, as Dr. Hoyt has found. Ours, however, were prepared from the liquid melt with the addition of ferrochrome and therefore are quite a different breed of inclusions. Under ordinary light, however, one would have supposed them identical.

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Corrosion Tests in Various Refinery Services

BY J. E. POLLOCK,* E. CAMP* AND W. R. HICKS*

(New York Meeting, February, 1935)

IN the oil-refining industry, steel comprises by far the greatest proportion of the materials used in construction work, but with an enormous number of alloy steels and nonferrous alloys available, and a greater knowledge of their properties and corrosion resistance, a substitution first in the "hot spots" and then in locations of moderately severe corrosive conditions will be made as the greater expense can be justified. In new construction work, advantage is taken of the experience already gained and appropriate materials used, whether for high temperatures and pressures demanding additional strength or for corrosive conditions. The locations, however, where equipment in operation constantly requires replacement will soon become evident, as will the necessity for replacement in more resistant materials, if considerable down-time is to be avoided.

In what direction and how far to go in the matter of alloys then becomes a question of the highest importance. Obviously, any replacement with more costly material must be justified economically by the promise of longer life, thereby saving both material and installation costs besides the reduction of loss of production. Where the equipment is overcapacity and a regular schedule of cleaning periods is in force, the last item frequently must be ruled out and justification made on the basis of the first two only. Installation of material that will outlast the remainder of the equipment and have no recovery value must also be avoided; this is particularly important in temporary construction or in old equipment that will soon become obsolete.

TEST METHODS

Either one of two methods or a combination of both, in the absence of reliable data in similar services, may be adopted to determine to what extent replacement with other, and perhaps more expensive, materials is justified. A unit may be constructed incorporating different metals or alloys so that comparative service may be obtained under the same service conditions; this has been applied in many instances, such as condenser and tank construction, but the opportunities for inspection may be few and

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* Humble Oil & Refining Co., Baytown, Texas.

far between. Besides, it is not always possible to obtain the full service life out of the moderately resistant metals because of the necessity for renewal of such parts as have not quite failed at such time as first renewals are made, in order to avoid a later shut-down period. Again, after considerable care has been taken with an installation, it has occurred that a unit has been taken out of service or even scrapped and dismantled without adequate data being obtained. These points, together with the difficulty of varying such construction except when locally produced, have contributed much towards influencing test work in the direction of the exposure of small test strips. A disadvantage, of course, of such a procedure is apparent in that the test is not carried out under actual service conditions usually in regard to temperature; the results, however, are comparative and, particularly when the metal in use is included as a standard, they can be of considerable value. Such tests can be carried out cheaply and their duration depends solely on the accessibility of the test strips.

ASSEMBLY OF DATA

Results of such metal tests obtained over a number of years in various refinery services are given in Table 1. The tests were made possible only by the kind cooperation of manufacturers who supplied specimen strips of their products; the arrangement of the metals in general is in groups as supplied, numbering being most easily effected in this way for recognition during test work. Where more than one result therefore is available for the same type of alloy, a more general indication of its service is possible. In this regard, however, a variation may have been introduced during finishing; where such details as are significant have been supplied, they have been included.

TEST PROCEDURE

The A.P.I. method¹ of cleaning the strips after exposure was adopted; i.e., removing lightly adhering scale, wire-brushing before and after soaking in gasoline, removing corrosion products from pitted places, and finally, drying and polishing with a cotton cloth. Where scale, such as mill scale, was initially present, it was removed by sand blasting, if necessary, and the prepared samples held in a dessicator until weighed. Comparison with other cleaning methods, such as with ammonium citrate, did not appear to justify abandonment of the initial method adopted.

Exposures were made on glass-covered rods supported on racks, the metals being spaced by glass spacers and the test carried out over a sufficiently long period to obtain weighable differences on the majority of the metals, or sufficiently short to prevent the complete loss of the metals.

¹ American Petroleum Institute Tentative Code for Determination of Resistance to Corrosion of Metal Samples in Petroleum Refining Processes. 1930.

The results recorded as penetration in inches per year take no account of pitting as such, but only as average loss of metal; the condition, of course, can be noted or recorded. Table 2 shows that the average penetration value is not independent of the length of the test. The samples used to determine the variation with time were two steels and a cast iron. Twelve specimens of each were placed on test in a condenser box and examinations were made in turn at monthly intervals, so that results were obtained for continuous periods of one, two, three months and so on up to 12 months. Each sample when inspected, cleaned and weighed was returned to the test for examination at the end of the 12 months. The data (Table 2) show that the penetration becomes less with time, the same effect being observed for the complementary periods. It would appear in this instance that corrosion proceeds fairly rapidly at first and becomes slower as a corroded layer or oxide coating is formed; it is also conceivable, and the data indicate it, that after a time the rate becomes almost uniform. The period of test therefore is important in regard to actual penetration, but it is less important when a standard reference specimen is used, since comparative results are obtained, which may be compared through the standard with other test data in the same or other services.

SERVICES AND CONDITIONS

The services chosen for test work were selected because of the amount of material involved in such a service, or because of the severity, as judged by the necessity for replacement of portions of the equipment. Summarized shortly, these and the test conditions are given in Table 3.

In general, for the test work indicated, it is unnecessary to know the exact conditions, since the results are comparative only and the conditions change within varying limits during the test period. For instance, tanks of the same crude may vary in water content, resulting in different amounts of hydrochloric acid being carried overhead in distillation though the hydrogen sulfide may remain fairly constant. Again, in such locations as the water wash on acid-treated naphtha, the concentration of the acid in the water will depend on the thoroughness of separation of the acid following acid treatment and on the volume of water used. Therefore, while conditions have been noted, they must be interpreted very broadly, as it has not been possible to analyze samples at short intervals.

RESULTS

A general survey of the results indicates that fresh water and steam services are comparatively mild and that the high chrome-nickel types of steel are highly resistant to corrosion in the locations selected. The fresh water turned out to be practically free from oxygen and contained a layer of oil on the surface, which accounts for the particularly low

TABLE 1.—Results of Metal Tests in Various Corrosive Media at Baytown

| Metal Analyses | | | | | | | | | | | | | |
|----------------|---|----------|----------|-----------|----------|-----------|--------|-------|------|-----------------------|--|----------------------------------|--|
| Strip No. | Name | Chromium | Nickel | Manganese | Silicon | Carbon | Copper | Zinc | Tin | A.P.I. Classification | Miscellaneous | Lb. per Cu. In. | |
| 1 | Naval brass (cold-rolled) | | | | | | 63 | 35 | 2 | 1 43 | | 0 305 | |
| 2 | Naval brass (hot-rolled) | | | | | | 63 | 35 | 2 | 1 43 | | 0 304 | |
| 3 | Muntz metal (cold-rolled) | | | | | | 60 | 40 | | 1 43 | | 0 305 | |
| 4 | Muntz metal (hot-rolled) | | | | | | 60 | 40 | | 1 43 | | 0 305 | |
| 5 | Manganese bronze (cold-rolled) | | | 0 5 | | | 56 | 41 | 0 5 | 1 43 | Al 1, Fe 1 | 0 304 | |
| 6 | Manganese bronze (hot-rolled) | | | 0 5 | | | 56 | 41 | 0 5 | 1 43 | Al 1, Fe 1 | 0 304 | |
| 7 | Manganese brass (cold-rolled) | | | | | | 56 | 41 | | 1 43 | | 0 304 | |
| 8 | Manganese brass (hot-rolled) | | | | | | 56 | 41 | | 1 43 | | 0 304 | |
| 9 | Admiralty metal (see also No. 10) (cold-rolled) | | | | | | 70 | 29 | 1 | 1 43 | | 0 306 | |
| 10 | Admiralty metal (see also No. 9) (hot-rolled) | | | | | | 70 | 29 | 1 | 1 43 | | 0 306 | |
| 11 | Aluminum bronze (cold-rolled) | | | | | | 88-96 | 1 | | 1 41 | Al 2.3-10 5, Fe | 0 297 | |
| 12 | Aluminum bronze (hot-rolled) | | | | | | 94 2 | | | 1 41 | Al 5.5 | 0 297 | |
| 13 | Toncan iron | | | 0 35 | | 0 05 | 0 4 | | | 1 3 | Mn 0.07-0.15 | 0 285 | |
| 14 | Stainless steel (12-14 Cr type)—(see 22) | 13 14 | 0 196 | 0 4 | 0 282 | 0 11 | | | | 1 34 | S-0.03 P-0.02 S-0.017 P-0.014 | 0 279 | |
| 15 | Stainless steel (18-8 type)—(hot-rolled) | | | | | | | | | | | | |
| 16 | Stainless steel (18-8 type)—(hot-rolled) | 18 00 | 9 5 | | | 0 10 | | | | 1 34 | Pb 7.80 | 0 279 | |
| 17 | Cast bronze (regular valve metal) | | 0 21 | | | | 80 05 | 7 79 | 4 07 | 1 43 | Fe 1 1, Sb 0 05, Pb 1 12 | 0 317 | |
| 18 | Manganese bronze (cast) (valve stem) | | 0 02 | 0 126 | | | 58 28 | 37 92 | 0 86 | 1 43 | Pb 3.8, Sb 0.03 | 0 300 | |
| 19 | Cast bronze (acid metal) | | | | | | 85 55 | 10 56 | 1 4 | 1 4 | Pb 14.5, Sb 0.12 | 0 312 | |
| 20 | Cast bronze (acid metal) | | | | | | 78 22 | 7 07 | | 1 4 | | 0 318 | |
| 21 | Stainless steel (12-14 Cr type)—(valve trim) | 12 94 | 0 2 | | 0 11 | | | | | 1 34 | | 0 279 | |
| 22 | Stainless steel (12-14 Cr type)—(valve trim) | | | | | | | | | | | | |
| 24 | Stainless steel (med. Cr type)—(valve trim)—(see No. 123) | 15-16 | | 0 24 | 0 24 | 0 07 | | | | 1 31 | | 0 277 | |
| 26 | Stainless steel (18-8 type) | 8-10 | 17-19 | 0 2-0 4 | 0 5 max. | 0 3-0 4 | | | | 1 34 | S & P 0.025 max. | 0 280 | |
| 27 | Stainless steel (18-8 type) | 17-19 | 7-9 | 0 2-0 4 | 0 5 max. | 0 25 max. | | | | 1 34 | S & P 0.025 max. | 0 285 | |
| 28 | Stainless steel (12-14 Cr type) | 12-14 | 1-1 5 | 0 2-0 4 | 0 5 max. | 0 15- 2 | | | | 1 34 | S & P 0.025 max. | 0 280 | |
| 29 | Stainless steel (med. Cr type) | 10-18 | 0 1 max. | 0 2-0 4 | 0 5 max. | 0 12 max. | | | | 1 31 | S & P 0.025 max. | 0 280 | |
| 30 | Stainless steel (12-14 Cr type) | 11 5-13 | 0 1 max. | 0 2-0 4 | 0 5 max. | 0 12 max. | | | | 1 31 | S & P 0.025 max. | 0 280 | |
| 31 | Stainless steel (12-14 Cr type) (annealed) | 13 26 | 2 1 | | 0 1-18 | | | | | 1 34 | | 0 280 | |
| 32 | High Cr-Ni (18-8 type) (annealed) | 24-26 | 19-21 | 0 5-0 7 | 0 75-1 5 | 0 15- 25 | | | | 1 34 | S-0 035 P-0 035 S-0 048 P-0 01 S-0 048 P-0 01 S-0 029 P-0 008 | 0 279 0 283 0 283 0 283 | |
| 33 | Steel (blue annealed, o.h.) | | | 0 36 | 0 002 | 0 04 | Trace | | | 1 12 | Fe | 0 279 | |
| 35 | Steel (blue annealed, o.h., pickled) | | | 0 36 | 0 002 | 0 04 | Trace | | | 1 12 | Fe | 0 283 | |
| 37 | Steel (copper) (blue annealed, o.h.) | | | 0 38 | 0 041 | 0 06 | 0 23 | | | 1 3 | Fe | 0 283 | |
| 39 | Steel (copper) (blue annealed, o.h., pickled) | | | 0 38 | 0 041 | 0 06 | 0 23 | | | 1 3 | Fe | 0 283 | |
| 41 | Steel (blue annealed, Bessemer) | | | 0 23 | 0 005 | 0 07 | Trace | | | 1 12 | Fe | 0 283 | |

TABLE 1.—(Continued)

| Strip No. | Name | Chromium | Nickel | Manganese | Silicon | Carbon | Copper | Zinc | Tin | A.P.I. Classification | Miscellaneous | Lb. per Cu. In. |
|-----------|--|-----------|-----------|-----------|----------|-----------|--------|------|-----|-----------------------|--|-----------------|
| | | | | | | | | | | | | |
| 42 | Steel (blue annealed, Bessemer, pkld) | | | 0.23 | 0.005 | 0.07 | Trace | | | 1.12 | S—0.042 P—0.109 | 0.283 |
| 43 | Steel (copper) (blue annealed, Bessemer) | | | 0.49 | 0.004 | 0.07 | 0.14 | | | 1.3 | S—0.062 P—0.096 | 0.283 |
| 44 | Steel (copper) (blue annealed, Bessemer, pkld) | | | 0.50 | 0.004 | 0.07 | 0.14 | | | 1.3 | S—0.062 P—0.096 | 0.283 |
| 45 | Steel (red hard, Bessemer) | | | 0.54 | 0.012 | 0.26 | Trace | | | 1.12 | S—0.035 P—0.099 | 0.283 |
| 46 | Steel (red hard, Bessemer, pkld) | | | 0.54 | 0.012 | 0.26 | Trace | | | 1.12 | S—0.035 P—0.099 | 0.283 |
| 47 | Steel (copper) (galvanized, Bessemer) | | | 0.33 | 0.005 | 0.08 | 0.15 | | | 2.1 | S—0.023 P—0.009 | 0.283 |
| 48 | Steel (copper) (galvanized, Bessemer, pkld) | | | 0.33 | 0.005 | 0.08 | 0.15 | | | 2.1 | S—0.023 P—0.009 | 0.283 |
| 49 | Steel (copper) (galvanized, Bessemer, pkld) | | | 0.48 | 0.004 | 0.09 | 0.05 | | | 2.1 | S—0.043 P—0.054 | 0.283 |
| 50 | Steel (copper) (galvanized, Bessemer, pkld) | | | 0.35 | 0.042 | 0.12 | 0.03 | | | 2.1 | S—0.043 P—0.054 | 0.283 |
| 51 | Steel (copper) (galvanized, Bessemer, pkld) | | | 0.4 | 0.003 | 0.13 | 0.2 | | | 2.1 | S—0.043 P—0.054 | 0.283 |
| 52 | Steel (long term coated) | | | 0.4 | 0.003 | 0.13 | 0.2 | | | 2.1 | S—0.043 P—0.054 | 0.283 |
| 53 | Steel (nickel electroplated) | Coating | Coating | 0.38 | 0.032 | 0.1 | 0.08 | | | 2.11 | (Ni 1.53 Oz./Sq. Ft.) S—0.034 P—0.06 | 0.283 |
| 54 | Steel (CR-Ni electroplated) | Coating | Coating | 0.57 | 0.004 | 0.12 | 0.03 | | | 2.11 | (Cr 0.47) (Ni 1.48 Oz./Sq. Ft.) S—0.045 P—0.01 | 0.283 |
| 55 | Stainless steel (18-8 type) | 15.55 | 11.18 | 0.8-0.9 | 1.25-1.5 | 0.08-0.16 | 1-1.5 | | | 1.34 | | 0.284 |
| 56 | pkld-qnhd @ 2100° F. | 7.5-9 | 21.5-23.5 | 0.8-0.9 | 1.25-1.5 | 0.08-0.16 | 1-1.5 | | | 1.34 | | 0.287 |
| 57 | Stainless steel (18-8 type)—(heat-treated and pkld) | 17-20 | 7-10 | 0.3-0.6 | 0.3-0.6 | 0.15 max. | | | | 1.34 | | 0.284 |
| 58 | High Cr-Ni alloy | 19 | 32 | 0.72 | 0.77 | 0.13 | | | | 1.34 | | 0.290 |
| 59 | High Cr-Ni alloy | 31.72 | 20.0 | 0.72 | 0.83 | 0.1 | | | | 1.34 | | 0.290 |
| 60 | High Cr-Ni alloy | 8.26 | 21.9 | 0.97 | 1.0 | 0.48 | | | | 1.34 | | 0.306 |
| 61 | Stainless steel (8-18 type) | 58.6 | 21.9 | 0.43 | 1.52 | 0.25 | | | | 1.34 | | 0.280 |
| 62 | High Cr-Ni W. alloy | 12.75 | 0.27 | 0.28 | 0.1 | 0.07 | | | | 1.34 | | 0.280 |
| 63 | Stainless steel (medium Cr type) | 20.86 | | 0.39 | 0.35 | 0.06 | | | | 1.31 | | 0.280 |
| 64 | Stainless steel (high Cr type) | 27.18 | | 0.41 | 0.42 | 0.08 | | | | 1.31 | | 0.280 |
| 65 | Stainless steel (8-18 type) | 6.75-7.75 | 18.8-19.9 | 0.5-0.7 | 0.8-1.4 | 0.42-0.48 | | | | 1.34 | | 0.288 |
| 66 | Stainless steel (8-18 type) | 6.75-7.75 | 18.8-19.9 | 0.5-0.7 | 1.0-1.4 | 0.1-0.2 | | | | 1.34 | | 0.288 |
| 67 | Stainless steel (18-8 type) | 17.8-18.8 | 7.75-9.0 | 0.35-0.5 | 0.4-0.7 | 0.2 max. | | | | 1.34 | | 0.285 |
| 68 | Cast iron, plain | | | 0.95 | 2.61 | 1.75 | | | | 1.11 | | 0.285 |
| 69 | Cast iron, alloy | | | 0.47 | 2.17 | 2.78 | | | | 1.11 | | 0.285 |
| 70 | Steel (copper) (high sulfur) | | 12.41 | 0.47 | 2.17 | 2.78 | | | | 1.11 | | 0.285 |
| 71 | Steel (copper) (high sulfur) | | | 0.35 | 0.009 | 0.07 | | | | 1.3 | | 0.270 |
| 72 | Steel (copper) (extra refined) | | | 0.13 | 0.005 | 0.04 | | | | 1.3 | | 0.283 |
| 73 | Steel (copper) | | | 0.45 | 0.008 | 0.07 | | | | 1.3 | | 0.283 |
| 74 | Steel (copper) | | | 0.45 | 0.008 | 0.07 | | | | 1.3 | | 0.283 |
| 75 | Stainless steel (12-14 Cr type)—(ann-pkld-wh) (see No. 79) | 12-13 | 0.4-0.5 | 0.4-0.6 | 0.4 max. | 0.07-0.12 | | | | 1.34 | | 0.281 |
| 76 | Stainless steel (high Cr type) | 20 | 8.5-9.5 | 0.5 max. | 0.3 max. | 0.15 max. | | | | 1.34 | | 0.278 |
| 77 | Stainless steel (18-8 type) | 17-19 | | | | | | | | 1.34 | | 0.281 |
| 78 | Stainless steel (12-14 Cr type) | 14 | | | | 0.1 | | | | 1.31 | | 0.279 |

TABLE 1.—(Continued)

| Metal Analyses | | | | | | | | | | | | | |
|----------------|--|----------|-----------|-----------|-----------|-----------|----------|-------|------|-----------------------|-----------------------|---------------|--|
| Strip No. | Name | Chromium | Nickel | Manganese | Silicon | Carbon | Copper | Zinc | Tin | A.P.I. Classification | Miscellaneous | Lb per Cu. In | |
| 79 | Stainless steel (12-14 Cr type)—(annealed and cleaned) (see No. 75)..... | 12-14 | 0 4 | | | 0 1 | | | | 1 34 | | 0 281 | |
| 82 | Valve metal..... | | | | | | 86 | 4 | 7 | 1 4 | Pb 3 | 0 319 | |
| 85 | Copper-silicon alloy, sheet..... | | | 1 03 | 3 04 | | 95 94 | | | 1 4 | Fe 0 2 | 0 306 | |
| 86 | Copper-nickel alloy, sheet..... | | 20 12 | 0 29 | | | 74 54 | 5 05 | | 1 42 | | 0 319 | |
| 87 | Copper-nickel alloy, sheet..... | | 28 84 | 0 58 | | | 64 73 | 5 85 | | 1 42 | | 0 320 | |
| 88 | Copper, sheet..... | | | | | | | | | 1 22 | | 0 321 | |
| 89 | Red brass, sheet..... | | | | | | 85 25 | 14 7 | | 1 4 | Cu plus Ag 99.96 | 0 315 | |
| 91 | Drawing brass, sheet..... | | | | | | 67 09 | 32 89 | | 1 4 | Fe 0 03 | 0 306 | |
| 92 | Tobin bronze, sheet..... | | | | | | 59 98 | 39 28 | 0 69 | 1 4 | Fe 0 01, Pb 0 01 | 0 303 | |
| 93 | Stainless steel (med. Cr type) ... | 15-18 | 0.25 max. | 0.5 max. | 1.2 max. | 0.12 max. | | | | 1 31 | S & P 0 03 max | 0 284 | |
| 95 | High Cr-Ni alloy | 21-24 | 12 | | | | 3 | | | 1 34 | | 0 284 | |
| 98 | Nickel-silicon alloy (not machinable) | | 85 | | 10 | | | | | 1 4 | Al 1 5 | 0 282 | |
| 99 | Cr-Ni-Mo-W alloy | 14 | 58 | | | | | | | 1 34 | Mo 17, W 5, Fe 6 | 0 318 | |
| 100 | Nickel-molybdenum alloy | | 60 | | | | | | | 1 4 | Mo 20, Fe 20 | 0 318 | |
| 101 | Copper-nickel alloy | | 67 app'x | 0 5-1.0 | 1 0-1.5 | 0 15-0 20 | 29 app'x | | | 1 42 | Fe 1.50-2.50 | 0 320 | |
| 102 | Nickel sheet, pure | | 97 app'x | | 1 0-1.5 | 0 15-0 25 | | | | 1 24 | Fe 1.0-1.5 | 0 320 | |
| 103 | Cr-Ni-Si alloy | 12 | 35 | | 5 | 0 25 | | | | 1 34 | | 0 283 | |
| 107 | High nickel-chromium alloy | 19 5 | 77 5 | 2 | | 1 20 | | | | 1 34 | Fe 1 max. | 0 307 | |
| 108A | Stainless steel (med. Cr type) | 17 | | | 0 5-1 | 0 25 | | | | 1 31 | | 0 280 | |
| 109 | Stainless steel (low Cr type) (see No. 129) | | | | | | | | | | | | |
| 111 | High Cr-Ni alloy Ni-Cr | 4 85 | 35-38 | 0 35 | 0 019 | 0 18 | | | | 1 31 | S-0.021 P-0.016 | 0 281 | |
| 116 | Cast iron, alloy | 16-19 | | | | | | | | 1 34 | | 0 285 | |
| 117 | Cast iron, alloy | 0 2-0 3 | 0 3-0 5 | 0 6-0 7 | 2 35-2 50 | 3 2-3 4 | | | | 1 11 | S-0 1 max. P-0.2 max. | 0 263 | |
| 122 | Stainless steel (see Nos. 178 & 180) | 1 3-4 0 | 12-15 | 1 0-1 2 | 2 0-2 5 | 2 8-3 0 | 5 0-7 0 | | | 1 11 | S-0.1 max. P-0.2 max | 0 265 | |
| 123 | Stainless steel (med. Cr type) (annealed) | 17 48 | | 0 36 | 0 29 | 0 64 | | | | 1 31 | S-0 021 P-0 018 | 0 280 | |
| 124 | Stainless steel (high Cr type) (annealed) | 15 50 | | 0 24 | 0 24 | 0 07 | | | | 1 31 | S-0.02 P-0.02 | 0 280 | |
| 125 | Wrought iron (special puddled) (see No. 140) | 19 37 | | 0 37 | 0 13 | 0 08 | | | | 1 31 | S-0 021 P-0 013 | 0 280 | |
| 126 | Wrought iron (genuine puddled) (see No. 140) | | 1 565 | 0 02 | 0 149 | 0 025 | 0 56 | | | 1 13 | S-0 019 P-0.158 | 0 278 | |
| 127 | Wrought iron (charcoal iron) (see No. 140) | | | 0 031 | 0 116 | 0 016 | | | | 1 13 | S-0.022 P-0 213 | 0 278 | |
| 129 | Stainless steel (low Cr type) (see No. 109) | | | 0 044 | Trace | 0 02 | 0 079 | | | 1 13 | S-0 018 P-0.036 | 0 278 | |
| 131 | High Cr-Ni alloy | 6 55 | | | | | | | | 1 31 | | 0 286 | |
| 132 | Copper-tin alloy | 25 | 35 | | 0 35 | 0 14 | | | | 1 34 | | 0 286 | |
| 133 | Copper-tin-nickel alloy | | 18 7 | | | | 88 | 12 | 5 72 | 1 42 | Fe 0.47 Pb 1.16 | 0 317 | |
| | | | | | | | 72 44 | 1 12 | | | | 0 318 | |

TABLE 1.—(Continued)

| Strip No. | Name | Chromium | Nickel | Manganese | Silicon | Carbon | Copper | Zinc | T _m | A P I Classification | Miscellaneous | Lb. per Cu. In. |
|-----------|--|----------|---------|-----------|---------|----------|--------|------|----------------|----------------------|------------------------------------|-----------------|
| | | | | | | | | | | | | |
| 134 | Copper-nickel alloy | | 27.94 | | 0.72 | | 65.62 | | 12 | 1.42 | Fe 5.04 | 0.319 |
| 135 | Copper-nickel alloy | | 52 | | | | 36 | | | 1.43 | Fe 1 | 0.312 |
| 136 | Stainless steel (18-8 type) | 18 | 8 | | | Low | | | | 1.34 | | 0.285 |
| 140 | Wrought iron (see Nos. 125, 126, 127) | | | 0.017 | 0.08 | 0.001 | 0.118 | | | 1.33 | Slag 2.87 S—0.011 P—0.079 | 0.282 |
| 147 | High Cr-Ni alloy (hot-rolled) | 22 | 22 | 2.5 | 0.3 | | | | | 1.34 | Fe 43 | 0.283 |
| 148 | High Cr-Ni alloy | 16 | 50 | 2 | | | | | | 1.34 | Fe 23 | 0.295 |
| 149 | High Cr-Ni alloy (casting material) | 20 | 32 | 2.5 | 2 | | | | | 1.34 | Fe 43.5 | 0.283 |
| 154 | High Cr-Ni alloy | 23.75 | 9.11 | | | 0.12 | | | | 1.34 | | 0.284 |
| 155 | High Cr-Ni alloy | 20.26 | 13.93 | | | 0.11 | | | | 1.34 | | 0.284 |
| 157 | High Cr-Ni alloy | 27 | 10.73 | | | 0.059 | | | | 1.34 | | 0.283 |
| 158 | Cast bronze | | | | | | 88 | | 10 | 1.4 | Pb2 | 0.283 |
| 170 | Stainless steel (med. Cr type) | 17.45 | | 0.36 | 0.33 | 0.11 | | | | 1.31 | S—0.017 P—0.021 | 0.286 |
| 172 | Aluminum bronze (hard) | | | 0.42 | 1.7 | 3.51 | 90 | | | 1.41 | Al 10 | 0.268 |
| 173 | Cast iron (class 150) | | | | | | | | | 1.11 | P.C. 3.51—C.C. 0.54—S—0.077 P—0.79 | 0.263 |
| 174 | High Cr-Ni alloy (calorized) | 15, in. | 35 min. | | | | | | | 1.34 | Fe, Zr, etc. | 0.285 |
| 175 | Stainless steel (18-8 type) (calorized) | 20 min. | 8 min. | | | | | | | 1.34 | Fe, Zr, Al, etc. | 0.285 |
| 176 | High Cr-Ni alloy (calorized) | 17-20 | 64-68 | | | | | | | 1.34 | Fe, Zr, Al, etc. | 0.280 |
| 177 | Stainless steel (med. Cr type) | 17.5 | 0.35 | 0.45 | | 1.05 | | | | 1.34 | | 0.280 |
| 178 | Cast iron, alloy (see No. 117) | 13.46 | 0.79 | 0.79 | 1.88 | 3.10 | 6.26 | | | 1.1 | | 0.265 |
| 179 | Cast iron, alloy | 2.57 | 1-4 | | | | | | | 1.1 | Fe | 0.265 |
| 195 | Cast aluminum | | | | | | | | | 1.21 | | 0.098 |
| 198 | Copper-tin-silicon alloy | | | | 1 | | 97 | | 2 | 1.4 | | 0.320 |
| 199 | Electric furnace iron, pure | | | | | | | | | 1.12 | | 0.284 |
| 200 | Anti-acid metal | | | | | | | | | 1.4 | | 0.284 |
| A-3 | Bronze | | | | | | 77 | | 8 | 1.4 | Pb 15 | 0.317 |
| A-9 | Bronze | | | | | | 88 | | 10 | 1.4 | | 0.311 |
| 45A | Aluminum bronze | | | | | | 89 | | | 1.41 | Al 10, Fe 1 | 0.270 |
| 50A | Copper-nickel alloy | | | | | | | 2 | | 1.42 | | 0.290 |
| 201 | Wrought iron (see Nos. 125, 126, 127, 140) | | | | | | | | | 1.13 | Contains Beryllium P—0.1 | 0.278 |
| 202 | Cast iron (see No. 173) | | | 0.3-0.5 | | C < 0.25 | | | | 1.11 | | 0.261 |
| 203 | Steel, carbon (used as standard) | | | | | | | | | 1.12 | P and S < 0.04 P 0.012 | 0.283 |
| 204 | Steel, locomotive firebox (used as standard) | | | | | | | | | 1.12 | | 0.278 |
| 205 | Steel, alloyed (nitrided) | 1.5 | | 0.50 | 0.028 | 0.12 | | | | 1.10 | Al 1.25, Mo 0.2 | 0.284 |
| 206 | Cast iron, high alloy | | | 0.35 | 14.5 | 0.3-0.4 | | | | 1.33 | S—0.08 max. P—0.02 max. | 0.253 |
| 220 | Aluminum-iron alloy | | | | | 0.85 | | | | 1.3 | Al 28.03, Fe 70.57 | 0.230 |
| 221 | Lead, commercial | | | | | 0.377 | | | | 1.23 | | 0.411 |

TABLE 1.—(Continued)

| Results of Metal Tests in Various Corrosive Media | | | | | | | | | | | | | | | | | | |
|---|--------------------------|----------------------------------|----------------------------------|---------------------|-------------------------------|--------------------------------|--|-----------------------------------|------------------------------------|--------------------------------|--|-------------------------------------|----------------------------------|---|--|--|---|--|
| Test No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 10A | 11 | 12 | 13 | 14 | 15 | 16 | 17 |
| Strip No. | Fresh Water, Pen. In./Yr | Salt Water Con-Box, Pen. In./Yr. | Salt Water Con-Box, Pen. In./Yr. | Steam, Pen. In./Yr. | Crude-oil Vapor, Pen. In./Yr. | Naphtha (Liquid), Pen. In./Yr. | Crack- ing Coil Bubble Tower, Pen. In./Yr. | Debu- tanizer Vapor, Pen. In./Yr. | Debu- tanizer Liquid, Pen. In./Yr. | HCl 5%, 1.3700 N, Pen. In./Yr. | HCl 5%, plus Acid Sludge, Pen. In./Yr. | Plant Cause, 30 2" B6, Pen. In./Yr. | Plant Cause, 20" B6, Pen. In./Yr | Wash Water from Treathers, Pen. In./Yr. | Separated Water from Straight Run Naphtha, Pen. In./Yr | Run Naphtha, Acid Treated, Pen. In./Yr | Run Naphtha, Acid Treated, Still, Pen. In./Yr | Run Naphtha, Acid Treated (Liquid), Pen. In./Yr. |
| 43 | 0.0026 | 0.0046 | 0.0055 | 0.0019 | 0.0175 | 0.0036 | 0.0118 | | | | | | | | | | | |
| 44 | 0.0059 | 0.0047 | 0.0042 | 0.0023 | 0.0052 | 0.0064 | 0.0115 | | | | | | | | | | | |
| 45 | 0.0025 | 0.0060 | 0.0044 | 0.0031 | 0.0032 | 0.0031 | 0.0099 | | | | | | | | | | | |
| 46 | 0.0119 | | 0.0041 | 0.0034 | 0.0039 | 0.0054 | 0.0124 | | | | | | | | | | | |
| 49 | 0.0009 | 0.0034 | 0.0023 | 0.0026 | 0.0024 | 0.0068 | 0.0018 | | | | | | | | | | | |
| 50 | 0.0006 | 0.0034 | 0.0050 | 0.0026 | Nil | 0.0056 | 0.0019 | | | | | | | | | | | |
| 51 | 0.0014 | 0.0035 | 0.0034 | 0.0018 | 0.0024 | 0.0044 | 0.0063 | | | | | | | | | | | |
| 52 | 0.0012 | 0.0066 | 0.0045 | 0.0012 | 0.0060 | 0.0042 | 0.0134 | | | | | | | | | | | |
| 53 | 0.0002 | 0.0018 | 0.0029 | 0.0002 | 0.0127 | 0.0020 | 100% | | | | | | | | | | | |
| 54 | 0.0004 | 0.0054 | 0.0031 | 0.0001 | 0.0158 | 0.0031 | 0.0190 | | | | | | | | | | | |
| 55 | Nil | Nil | 0.0001 | Nil | Nil | 0.0036 | 0.0002 | | | | | | | | | | | |
| 56 | Nil | 0.0029 | 0.0023 | Nil | 0.0315 | 0.0031 | 0.0037 | | | | | | | | | | | |
| 57 | Nil | Nil | 0.0003 | Nil | 0.0004 | 0.0028 | 0.0001 | | | | | | | | | | | |
| 58 | Nil | Nil | 0.0001 | Nil | Nil | 0.0022 | 0.0001 | | | | | | | | | | | |
| 59 | Nil | 0.0031 | 0.0015 | Nil | 0.0001 | 0.0029 | 0.0002 | | | | | | | | | | | |
| 60 | Nil | Nil | 0.0001 | Nil | Nil | 0.0011 | Nil | | | | | | | | | | | |
| 61 | Nil | 0.0032 | 0.0024 | Nil | 0.0187 | 0.0027 | 0.0011 | | | | | | | | | | | |
| 63 | Nil | 0.0008 | 0.0006 | Nil | 0.0001 | 0.0014 | 0.0006 | | | | | | | | | | | |
| 64 | Nil | 0.0038 | 0.0017 | Nil | 0.0013 | 0.0050 | 0.0005 | | | | | | | | | | | |
| 65 | Nil | 0.0021 | 0.0028 | Nil | 0.0008 | 0.0043 | 0.0004 | | | | | | | | | | | |
| 66 | Nil | Nil | Nil | Nil | 0.0007 | 0.0039 | 0.0002 | | | | | | | | | | | |
| 67 | Nil | 0.0100 | 0.0019 | 0.0001 | 0.0001 | 0.0025 | 0.0021 | | | | | | | | | | | |
| 68 | Nil | 0.0033 | 0.0017 | 0.0001 | 0.0118 | 0.0023 | 0.0007 | | | | | | | | | | | |
| 69 | Nil | 0.0006 | 0.0002 | 0.0001 | 0.0005 | 0.0010 | 0.0002 | | | | | | | | | | | |
| 70 | 0.0005 | 0.0044 | 0.0044 | 0.0024 | 0.0136 | 0.0111 | 0.0054 | | | | | | | | | | | |
| 71 | Nil | 0.0078 | 0.0045 | 0.0020 | 0.0046 | 0.0053 | 0.0001 | | | | | | | | | | | |
| 72 | 0.0033 | 0.0048 | 0.0048 | 0.0020 | 0.0124 | 0.0053 | 0.0135 | | | | | | | | | | | |
| 73 | 0.0041 | 0.0072 | 0.0048 | 0.0021 | 0.0030 | 0.0044 | 0.0097 | | | | | | | | | | | |
| 74 | 0.0027 | 0.0055 | 0.0046 | 0.0018 | 0.0023 | 0.0036 | 0.0124 | | | | | | | | | | | |
| 75 | Nil | 0.0037 | 0.0015 | Nil | 0.0005 | 0.0047 | 0.0008 | | | | | | | | | | | |
| 76 | Nil | Nil | 0.0001 | Nil | 0.0003 | 0.0028 | 0.0001 | | | | | | | | | | | |
| 77 | Nil | Nil | 0.0001 | Nil | Nil | 0.0076 | Nil | | | | | | | | | | | |
| 78 | Nil | 0.0049 | 0.0020 | Nil | 0.0013 | 0.0046 | 0.0005 | | | | | | | | | | | |
| 79 | Nil | Nil | 0.0002 | Nil | 0.0002 | 0.0026 | 0.0002 | | | | | | | | | | | |
| 82 | 0.0013 | 0.0028 | 0.0017 | Nil | 0.0090 | 0.0347 | 0.1059 | | | | | | | | | | | |

TABLE 1.—(Continued)

| Results of Metal Tests in Various Corrosive Media | | | | | | | | | | | | | | | | | | |
|---|---------------------------|---|---|---------------------|-------------------------------|--------------------------------|--------------------------------------|----------------------------------|-----------------------------------|---------------------------------|--|--|------------------------------------|--|---|--|---|---|
| Test No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 10A | 11 | 12 | 13 | 14 | 15 | 16 | 17 |
| Strip No. | Fresh Water, Pen. In./Yr. | Salt Water Con-denser Box, Pen. In./Yr. | Salt Water Con-denser Box, Pen. In./Yr. | Steam, Pen. In./Yr. | Crude-oil Vapor, Pen. In./Yr. | Naphtha (Liquid), Pen. In./Yr. | Crack-ing Bubble Tower, Pen. In./Yr. | Debu-tanizer Vapor, Pen. In./Yr. | Debu-tanizer Liquid, Pen. In./Yr. | HCl, 5%, 1.3700 N, Pen. In./Yr. | HCl, 5% Sulfuric Acid Sludge, Pen. In./Yr. | Plant Caustic, 39 1/2 Be, Pen. In./Yr. | Plant Caustic, 20 Be, Pen. In./Yr. | Wash Water from Treaters, Pen. In./Yr. | Separated Water from Straight Run Naphtha, Pen. In./Yr. | Rerun Naphtha, Acid Treated, Lookbox, Pen. In./Yr. | Rerun Naphtha, Acid Treated, Still (Vapors), Pen. In./Yr. | Rerun Naphtha, Acid Treated, Still (Liquid), Pen. In./Yr. |
| 147 | Nil | 0.0007 | 0.0013 | 0.0001 | 0.0004 | 0.0029 | 0.0007 | | | | | | | | | | | |
| 148 | Nil | | Nil | 0.0001 | 0.0030 | 0.0015 | 0.0007 | | | | | | | | | | | |
| 149 | Nil | 0.0024 | 0.0010 | Nil | 0.0010 | 0.0022 | 0.0395 | | | 0.0193 | 0.0203 | | | | 0.0018 | | | |
| 154 | Nil | Nil | Nil | Nil | Nil | 0.0009 | 0.0001 | | | | | | | | 0.0021 | | | |
| 156 | Nil | Nil | Nil | Nil | Nil | 0.0005 | 0.0001 | | | 0.0180 | 0.0166 | | | | | | | |
| 157 | Nil | Nil | Nil | Nil | Nil | 0.0010 | 0.0001 | | | | | | | | | | | |
| 158 | 0.0018 | 0.0021 | 0.0025 | Nil | 0.0167 | 0.0214 | 100% | | | | | | | | | | | |
| 170 | | | 0.0033 | 0.0025 | 0.0003 | 0.0065 | 0.0005 | | | | | | | | | 0.0049 | | |
| 172 | | | 0.0012 | 0.0031 | 0.0031 | 0.0189 | 0.0585 | | | | | | | | | | | |
| 173 | | | 0.0046 | 0.0046 | 0.0090 | 0.0084 | 0.0051 | | | | | | | | | | | |
| 174 | | | 0.0011 | 0.0011 | 0.0030 | Nil | 0.0006 | | | | | | | | | | | |
| 175 | | | 0.0018 | 0.0012 | 0.0007 | 0.0008 | 0.0004 | | | | | | | | | | | |
| 176 | | | 0.0012 | 0.0012 | 0.0031 | Nil | 0.0003 | | | | | | | | | | | |
| 177 | | | 0.0074 | 0.0074 | 0.0002 | 0.0015 | Nil | | | | | | | | 0.0140 | | | |
| 178 | | | 0.0029 | 0.0029 | 0.0130 | 0.0008 | Nil | | | 0.0520 | 0.0819 | | | | | | | |
| 179 | | | 0.0037 | 0.0037 | 0.0037 | 0.0120 | 0.0078 | | | | | | | | | | | |
| 198 | | | 0.0026 | | Nil | 0.0055 | 0.0034 | | | | | | | | | | | |
| 199 | | | | | | | | | | | | | | | | | | |
| 200 | | | | | | | | | | | | | | | | | | |
| A-3 | Nil | 0.0037 | 0.0028 | 0.0002 | 0.0084 | 0.0193 | 100% | | | 0.0340 | 0.0520 | | | | | 0.1270 | | |
| A-9 | 0.0003 | 0.0003 | 0.0016 | Nil | 0.0056 | 0.0033 | 0.0703 | | | 0.0389 | 0.0052 | | | | 0.0014 | | | |
| 50A | 0.0002 | 0.0001 | 0.0011 | Nil | 0.0183 | 0.0096 | 0.0376 | | | 0.1435 | 0.0098 | | | | 0.0057 | | | |
| 50A | 0.0001 | 0.0001 | 0.0004 | 0.0001 | 0.0040 | 0.0014 | 0.0078 | | | | | | | | 0.0095 | | | |
| 201 | 0.0001 | | | | 0.0081 | 0.0105 | 0.0054 | | | 1.3760 | 0.0478 | | | | | | | |
| 202 | | 0.0039 | 0.0039 | | 0.0378 | 0.0225 | 0.0122 | | | 10.1075 | 0.1514 | 0.0024 | 0.0008 | 0.0715 | | 0.1210 | 0.0014 | 0.0023 |
| 203 | 0.0002 | 0.0036 | | | | 0.0363 | 0.0132 | | | 0.0896 | 0.0508 | 0.0005 | 0.0002 | 0.1109 | 0.1070 | 0.1560 | 0.0048 | 0.0133 |
| 204 | | | 0.0046 | | 0.0388 | 0.0330 | 0.0132 | | | 0.1355 | 0.0456 | 0.0012 | 0.0003 | 0.0746 | 0.1219 | 0.1340 | 0.0051 | 0.0138 |
| 205 | Nil | 0.0045 | 0.0033 | 0.0044 | Nil | 0.0363 | 0.0041 | | | | | | | | | | | |
| 206 | 0.0028 | 0.0043 | 0.0020 | 0.0045 | 0.0055 | 0.0056 | 0.0014 | | | 0.0119 | 0.0358 | Nil | 0.0002 | 0.0376 | 0.0085 | 0.0001 | | |
| 220 | | | | | 0.0031 | | 0.0066 | | | | | | | | | | | |
| 221 | | | | | | | | | | | | | | | | | | |

† Badly pitted.

TABLE 3.—*Test Condition*

| Test | Service | Conditions | Period | Remarks |
|------|--|--|------------------|---|
| 1 | Fresh water (recirculated) | Temperature, 100° to 120° F. | 186 days | Open-type condenser box; oxygen content practically nil, due to surface film of oil on water. All penetration values low. |
| 2 | Salt water | Temperature, 100° to 120° F. | 164 days | Open-type condenser box; water, pH 8.5; NaCl, 4 to 4.5 grams per liter. |
| 3 | Salt water | Temperature 100° to 120° F. | 149 days | Conditions very similar to those of No. 2. |
| 4 | Steam | Pressure, 150 lb. per sq. in. | 206 days | Exposure made in vapor space of large steam trap. |
| 5 | Crude oil vapor | Atmospheric temperature | 195 and 175 days | Exposure made in vapor space of tank in light West Texas crude-oil service. Metals exposed in two groups; one removed after 175 days, other after 195 days, otherwise exposures were identical. Corrosive agents; oxygen, moisture and hydrogen sulfide. |
| 6 | Naphtha (straight run) | Atmospheric temperature | 125 days | Exposure made in run-down tank handling 375° and 400° straight-run naphtha. Corrosive agents: hydrogen sulfide, moisture and small amounts of HCl. |
| 7 | Naphtha vapor Cracking coil Bubble tower | Temperature, 350° F. Pressure, 90 lb. | 136 days | Exposure made below top plate of bubble tower. Corrosive agents: sulfur compounds (hydrogen sulfide, mercaptans), naphthenic acids. |
| 8 | Debutanizer vapor | Temperature, 220° F. Pressure, 90 lb. per sq. in. | 221 days | Vapor over top plate of debutanizer handling cracked naphtha. Corrosive agents: sulfur compounds (hydrogen sulfide, mercaptans), moisture, and possibly traces of naphthenic acids. |
| 9 | Debutanizer liquid | As for No. 8 | As for No. 8 | Liquid on top plate of debutanizer |
| 10 | Hydrochloric acid, 5 per cent | Room temperature | 24 hr. | Corrosive agent; hydrochloric acid used in cleaning scale from condensers, etc. |
| 10A | Hydrochloric acid, 5 per cent with acid sludge | Room temperature | 24 hr. | Corrosive agent; hydrochloric acid. Inhibitor: acid sludge (3 per cent) from naphtha treaters. |
| 11 | Caustic soda | Room temperature | 50 days | 39.2° B _é ; NaOH, 463 grams per liter; Na ₂ S, 17.6 grams per liter. |
| 12 | Caustic soda | Room temperature | 60 days | 20° B _é ; NaOH, 155 grams; Na ₂ S, 28 grams per liter. |
| 13 | Acid wash water | Atmospheric temperatures | 75 days | Nos. 11 and 12 were laboratory exposures without agitation. Typical analyses: (1) Total solids, 4.4 grams/liter; NaCl, 2.14; SO ₂ , 2.76; normality, 0.086. (2) SO ₂ , 1.29 grams/liter; SO ₃ , 0.574; normality, 0.055. |
| 14 | Separated water from crude naphtha | | 64 days | Water: pH 4.0; HCl, 0.847 grams/liter; H ₂ S, 0.017; total solids, 2.55. |
| 15 | Re-run naphtha | Temperature, 100° F. | 21 days | Naphtha is associated with acidic water; water is condensed from steam used in distillation and acid (SO ₂) is present as a decomposition product of acid esters. Separated water; pH less than 3.0; acidity equivalent to 0.58 to 2.02 grams per liter by methyl orange end point and 0.96 to 3.24 by phenolphthalein measured as KOH. Traces of sulfuric acid also present due to oxidation of SO ₂ . H ₂ S also present in small quantities. |
| 16 | Naphtha vapor in re-run still | Temperature, 315° F. | 50 days | Exposure in same still as 17 but in vapor space, 2 ft. above liquid level. |
| 17 | Naphtha in re-run still | Temperature, 315° F. | 50 days | Acid-treated naphtha caustic neutralized. Exposure 2 ft. from bottom of still. Corrosive agents, same as 15 except that at temperature of test the steam would be dry. |

corrosion rates. This indicates the efficacy of such a simple means of excluding air. Steam apparently is not very corrosive, so much of the trouble encountered with steam valves must be due to erosion rather than

corrosion, though the latter effect may become marked when oxygen and carbon dioxide are present.

The high chrome-nickels such as Nos. 32, 60, 99, 131, 154, 156 and 157 are particularly resistant in all the services; these in every case contain 25 per cent or more of chromium, with the exception of 99, and nickel varying from 9 to 58 per cent. No. 99, made up of 14 per cent chromium and 58 per cent nickel, contained 17 per cent molybdenum and 5 per cent tungsten. Of almost the same order of resistance are the 18-8 (chrome-nickel) steels such as 16, 55, 57, 58 and 136; these are all of low carbon content and the general effect of high carbon in lessening corrosion resistance may be observed by comparing the foregoing with 27, 68 and 69, which have carbon contents of 0.25 (max.) and 0.2 (max.) per cent. The disadvantage of buying merely an "18-8 type" metal without a knowledge of the carbon content is therefore indicated.

The 8-chrome, 18 nickel type, such as 26, 67 and 68, appears to rate approximately the same as the high-carbon 18-8 metals, while high-nickel low-chrome such as No. 63 (58.6 Ni, 11.44 Cr) and No. 107 (77.5 Ni, 19.5 Cr) show to less advantage than a KA₇ metal such as No. 32.

High-chrome, medium-chrome and 12-14 chrome steels definitely appear to be much less resistant than the KA₂S type; reference in this respect may be made to such specimens as 22, 24, 28, 29, 65, 78, 79, 93, 108A, 122 and 123, the effect being somewhat proportional to the chromium content. The low-chrome (4 to 6 per cent), typified by 109 and 129, leaves much to be desired for corrosion resistance, though it does show an advantage over steel, particularly where oxygen might be expected to play a considerable part, as in crude-oil storage. That better material could be chosen for that service, however, at reasonable comparative cost is evident from the results 49, 50 and 51 for galvanized stock and 195, aluminum.

While the high chrome-nickel alloys, KA₂S, KA₂ and high-chrome steels are in general very resistant to corrosion, they must not be looked upon as being capable of universal economic adoption. The small difference in price between KA₂S and a 12-14 chrome steel for small manufactured articles such as valve trim justifies standardizing on the former for any but the very mildly corrosive locations. In debutanizer service for plate material, 12-14 chrome steel lasted only 16 months; tests 8 and 9 show metal 24 (15-16 Cr) to be not particularly resistant to the liquid on a debutanizer plate. While the copper-nickel alloys were considered (see No. 101), replacement was made in cast iron and considerably longer service was obtained; the indicated effectiveness of an alloy cast iron is shown by No. 117 in this service.

Fig. 1 illustrates the improved resistance with increasing chromium content and the superiority of the 18-8 metal. Pitting of the lower chromium-content steels is illustrated. The metals shown were exposed to salt water for 164 days (test No. 2).

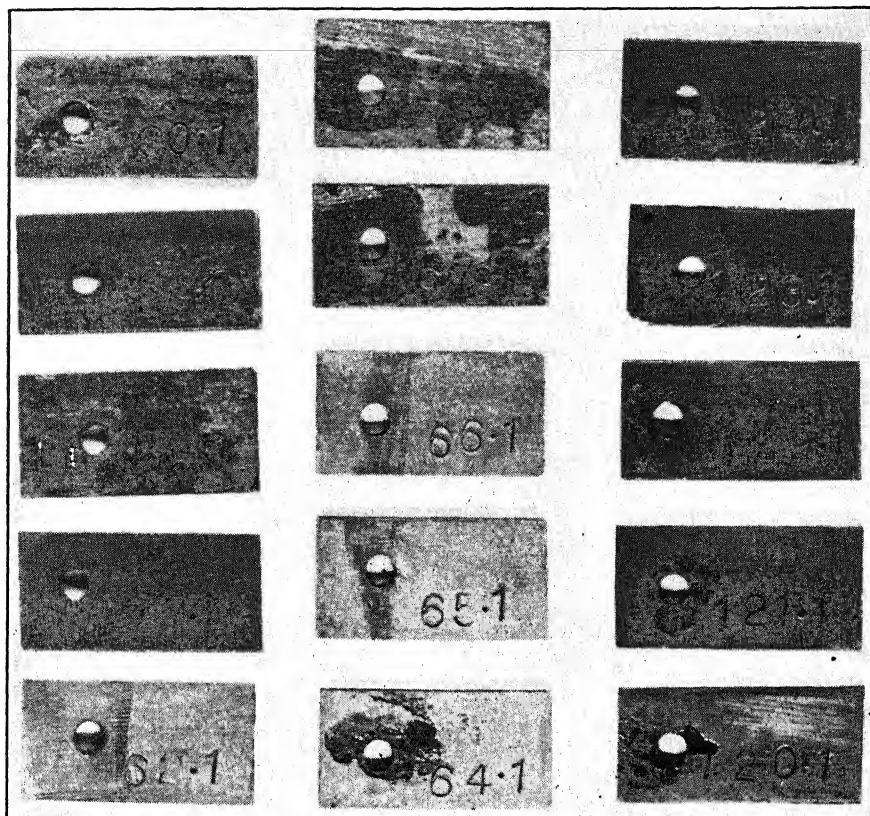


FIG. 1.—IMPROVEMENT IN RESISTANCE WITH INCREASING CHROMIUM CONTENT.

METALS EXPOSED TO SALT WATER (TEST No. 2)

| Strip No. | Analyses, Per Cent | | | | |
|--------------|--------------------|-----------|-----------|----------|-----------|
| | Chromium | Nickel | Manganese | Silicon | Carbon |
| 30 | 11.5-13.0 | 0.1 max. | 0.2-0.4 | 0.5 max. | 0.12 max. |
| 29 | 16-18 | 0.1 max. | 0.2-0.4 | 0.5 max. | 0.12 max. |
| 28 | 12-14 | 1.0-1.5 | 0.2-0.4 | 0.5 max. | 0.15-0.20 |
| 27 | 17-19 | 7-9 | 0.2-0.4 | 0.5 max. | 0.25 max. |
| 62 | 18.28 | 0.36 | 0.48 | 0.35 | 0.06 |
| 68 | 6.75-7.75 | 18.8-19.5 | 0.5-0.7 | 1.0-1.4 | 0.1-0.2 |
| 67 | 6.75-7.75 | 18.8-19.9 | 0.5-0.7 | 0.8-1.4 | 0.42-0.48 |
| 66 | 27.18 | | 0.41 | 0.42 | 0.08 |
| 65 | 20.86 | | 0.39 | 0.35 | 0.06 |
| 64 | 12.75 | 0.27 | 0.28 | 0.10 | 0.07 |
| 124 | 19.37 | | 0.37 | 0.13 | 0.08 |
| 123 | 15.50 | | 0.24 | 0.24 | 0.07 |
| 122 | 17.48 | | 0.36 | 0.29 | 0.64 |
| 121 | 11.52 | | 0.25 | 0.15 | 0.08 |
| 120 | 13.98 | | 0.27 | 0.26 | 0.35 |

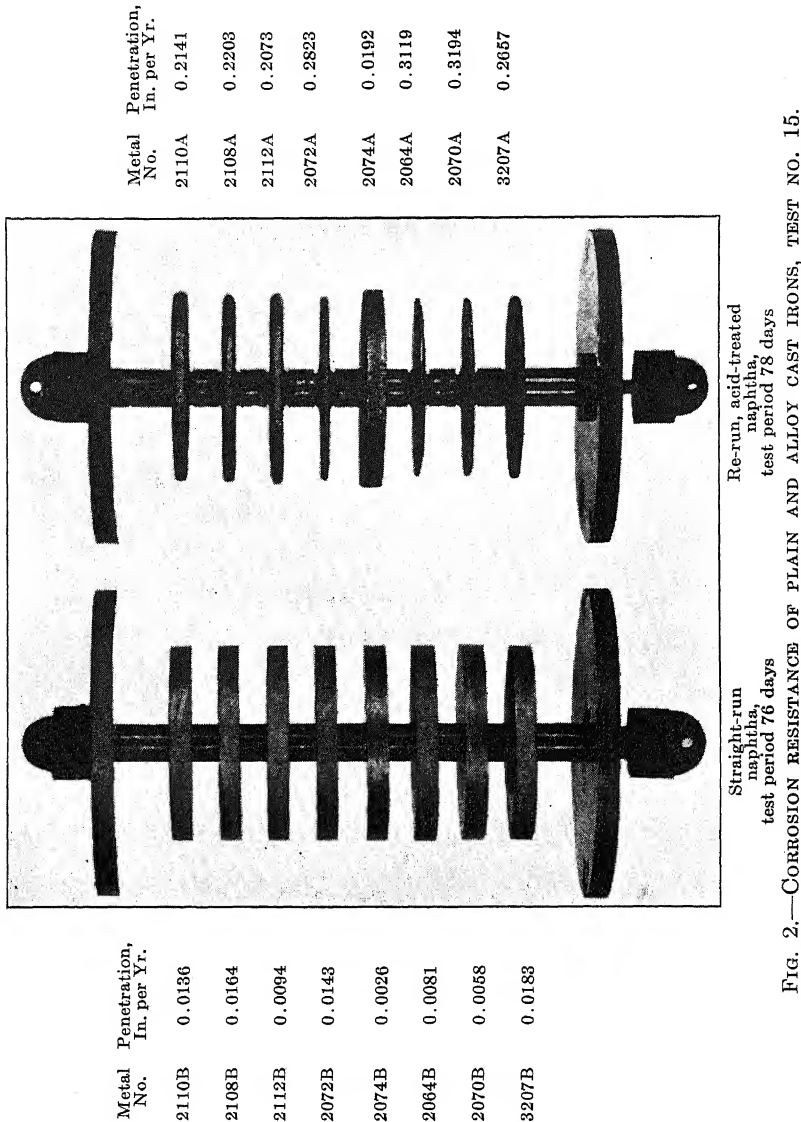


FIG. 2.—CORROSION RESISTANCE OF PLAIN AND ALLOY CAST IRONS, TEST NO. 15.

ANALYSES OF METALS SHOWN IN FIG. 2

| Type | Metal No. | Analyses, Per Cent | | | | |
|---------------------------|-----------|--------------------|------|------|------|------|
| | | Total C | Si | Ni | Cr | Cu |
| Nickel pipe iron..... | 2110 | 3.01 | 0.94 | 3.24 | | |
| Hard nickel-chromium..... | 2108 | 3.29 | 2.73 | 2.71 | 0.76 | |
| Chromium-nickel type..... | 2112 | 3.46 | 2.47 | 0.55 | 0.81 | |
| Ni-Cu-Cr iron..... | 2072 | 3.44 | 1.65 | 3.0 | 0.51 | |
| High Ni-Cu-Cr iron..... | 2074 | 3.11 | 1.51 | 13.7 | 2.32 | 1.25 |
| Nickel-chromium type..... | 2064 | 3.40 | 1.55 | 1.26 | 0.50 | 6.06 |
| Pipe iron..... | 2070 | 3.41 | 1.99 | | | |
| High-strength..... | 3207 | 2.81 | 1.86 | 2.07 | | |

Exposures in 5 per cent hydrochloric acid (test No. 10) indicate the comparative failure of the medium-chrome steels, 31, 123 and even an 18-8 such as 136, whereas the copper-nickel alloys 86, 87 and 101 show to better advantage, and the high-copper low-zinc alloys are definitely resistant to acidic conditions. The alloy cast irons 117 and 178 show a decided improvement over plain cast iron, though the silicon iron is outstanding in this test. In the cleaning of tubes with acid, sludge from acid-treating of naphthas has been used as an inhibitor. Tests 10 and 10A compare the action without and with sludge; a considerable reduction of attack is indicated in the case of the copper alloys and the plain cast iron (70 and 202); a distinct reduction is also obtained with wrought iron and steel, while in some cases, such as with alloy cast irons, no protection by the sludge is noted.

None of the metals tested in the caustic soda solutions showed high losses; the copper-nickel alloys, nickel sheet, 18-8 and 12-14 per cent chrome steels were better than the copper-tin alloys with lead added.

In very weak acid (sulfurous and sulfuric) such as wash water from acid-treating, the copper alloys (copper-zinc, copper-tin and copper-nickel) display considerable resistance. A similar resistance is shown to water (containing hydrochloric acid) separated from naphtha in the distillation of crude oil. The chrome-nickel and chrome steels, on the other hand, are seen to be resistant to wash water (79) but not to water separated from crude naphtha (27, 108A and 136), indicating a much greater resistance to dilute sulfuric and sulfurous acid than to dilute hydrochloric acid. Plain steel, wrought iron and cast iron are short-lived in such services; in water separated from straight-run naphtha a plain and a medium-chrome steel are shown as complete losses (test No. 14).

A set of plain and alloy cast irons is depicted in Fig. 2, showing the comparative effect of exposures in distillates from crude and from acid-treated naphtha.

Several steels showing different methods of treatment and modifications such as the inclusion of copper and varying amounts of carbon are included. Corrosion rates of these are comparatively high in such a series of alloys; it is obvious that isolated values should not be used.

Supplies of tank-steel specimens and of locomotive fire-box steel, S.A.E. 1020, have been used as standards in the test work.

Various discrepancies may be found in the data, but to anyone acquainted with corrosion test work such variations are not unusual, though attempts have been made to arrange the samples so that the conditions may be as uniform as possible for all samples. In the application of the results due consideration should be given to the manner in which the metal is to be used and its physical and chemical properties determined as suitable; contact of iron with aluminum in moist conditions

undoubtedly will prove detrimental to the aluminum because of the electrolytic action set up. Other cases are perhaps better known. While the physical properties should be suitable for the task, care should be exercised that these are not markedly changed during fabrication; hammering test strips has doubled the penetration value. A practical illustration of this is the very marked corrosion at the tong marks on underground pipe.

In the various locations where corrosion occurs, other methods than replacement with more expensive alloy must frequently be considered. Proper separation of water may frequently reduce corrosion to negligible proportions; neutralization of acidic conditions may prove more economical than expensive replacement where a large amount of equipment is involved.

It is not possible to give very detailed application of the results discussed but a few instances may be given as typical of their application. Replacement of steel nipples connecting running lines or gage columns to naphtha accumulators by KA_2S steel and alloy cast iron (Ni 14, Cu 6, Cr 2) has increased the life from a few months to at least over $2\frac{1}{2}$ years, as the last inspection indicates that the alloys are still in good condition. The substitution of brass or bronze and alloy cast iron such as Ni-Resist for plain steel and cast-iron liners in pumps, of KA_2S and brass pump rods, and of Monel impellers have all tended to give longer operating periods. In equipment for handling caustic soda, though more resistant metals are available, steel and cast iron will continue in general to be economical. Admiralty bundles give good service in condensers not subjected to acid conditions, but where an alkaline water containing oxygen is used, a higher copper alloy has been found advantageous.

While it has been impossible to discuss every metal, and it has not been the intention of the paper to draw attention to trade products but rather to consider trends with change of composition, it is hoped that the data presented may be of use both to users and manufacturers; to the former as an aid to standardization in the direction of more resistant materials, and to the latter as a means of standardizing products for stock purposes, and possibly, as a result of careful study, of indicating the probable trend for improvement of corrosion resistance of some of the alloys at not too great a cost. All trade names have been withdrawn from the tables, with the intention that composition be made the means of reference.

ACKNOWLEDGMENTS

Without the cooperation of the manufacturers it would have been impossible to collect such a number of metals as was used and without the cooperation of a number of colleagues it would have been impossible to collect such an amount of information, which has been accumulated

over a number of years. Special recognition is due to Messrs. W. J. Bernier, S. S. Frazer and F. Hederhorst, who shared in the actual work, to Mr. Brian Mead for its initiation, and to Dr. Sherman S. Shaffer for his advice during its progress. If the record should prove of any value to industry, the generous action taken by the Humble Oil and Refining Co. in permitting these data to be published will no doubt be appreciated.

DISCUSSION

(P. E. McKinney presiding)

H. D. WILDE, JR.,* Houston, Tex.—The authors realize that corrosive conditions in various refineries vary and that the results or conclusions that are drawn from these tests should be considered somewhat in the nature of generalizations; and that it will probably be necessary for people or workers in other refineries who are interested in the same problem to carry out similar tests. The paper does, however, illustrate a manner of attacking the problem that we have found very helpful in our own operations.

R. L. DUFF,† Elizabeth, N. J.—A test of this nature should be used as an indicator only. One can obtain all kinds of results from a test of this kind, different heat treatments of the material under test, corroding at different rates. If there has been any mechanical work done on the test pieces causing mechanical stresses to be present, this material will be corroded more rapidly than if it were in relief or properly annealed.

Numerous variables must be considered in selecting a metal for corrosion-resistant service; i.e., high or low temperature service and pressure. If it is high temperature, one must consider the stability of the alloy and if straight chromium alloys are used at elevated temperatures, one must be very careful because they lose their ductility and become very brittle under such conditions. Other points to be considered are machinability, weldability, coefficient of expansion, thermal conductivity, etc.

During 16 years with my company we have run numerous tests of this nature and the results obtained have been used only as an indicator of what might be expected. The only sure method to test out material is by actual service.

J. T. MACKENZIE,‡ Birmingham, Ala. (written discussion).—This paper contains a great deal of valuable work but it is difficult to follow through all of the tables to find what one wants. The writer is primarily interested in the comparative life of cast iron, plain steel, Ni-Resist and the stainless steel, and has picked out exposure conditions where comparable results can be obtained and assembled them in Table 4, which he believes will make easy reading for a great many people who are interested in the subject. The differences in performance of the several metals in different media show peculiar results; especially notable is the performance of the Ni-Resist as compared to the stainless in oils and vapors themselves. This is also the service in which cast iron seems to be much better than the plain steel.

Values given are averages of several tests, when possible, as several samples of each material were exposed.

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TABLE 4.—*Comparison of Four Metals*

| Corrosive Agent | Penetration in One Yr., In | | | | |
|--|----------------------------|-----------------|---------------------|----------------|--------------------|
| | Plain Carbon Steel | Plain Cast Iron | Ni-Resist Cast Iron | 18-8 Stainless | Time, Days Exposed |
| Fresh water | 0 0002 | 0 0002 | 0 0001 | Nil | 186 |
| Salt water | 0 0041 | 0 0045 | 0 0030 | 0 0004 | 149 |
| Acid wash water | 0 1269 | 0.2008 | 0 0285 | Nil | 56 |
| Water separated from naphtha | 0 1143 | 0 1141 | 0 0140 | 0.0310 | 25 |
| Crude-oil vapor | 0 0383 | 0 0086 | 0 0180 | 0 0002 | 195-197 |
| Naphtha liquid | 0.0448 | 0 0095 | 0 0015 | 0.0023 | 125 |
| Re-run naphtha | 0.0136 | 0 0023 | 0.0004 | 0.0001 | 21 |
| Cracking tower | 0 0132 | 0 0053 | 0 0011 | 0 0002 | 221 |
| HCl, 5 per cent | 0 1126 | 10 1075 | 0 0582 | 0 0532 | 1 |
| HCl, 5 per cent plus acid sludge | 0 0482 | 0 1514 | 0 0649 | 0 0517 | 1 |
| Plant caustic, 39.2° Bé | 0 0088 | 0 0024 | 0 0002 | 0 0001 | 50 |
| Plant caustic, 20° Bé | 0 0003 | 0 0008 | 0 0001 | Nil | 60 |
| Plant caustic, 15° Bé | 0 0004 | 0 0008 | 0 0002 | Nil | 77 |
| Plant caustic, 10° Bé | 0.0002 | 0 0001 | 0 0002 | Nil | 93 |

J. E. POLLOCK (written discussion).—The tables may be somewhat difficult to follow when the composition table is not opposite the penetration data. In our own case this difficulty has been overcome by matching photostats of the original tables.

In actually using the data, the service most nearly resembling the one on which data are required is scanned, and reference made to those metals showing little or no penetration and the general type determined. Depending on the location and the seriousness of the corrosion, a particular metal is chosen; the location will naturally determine whether that particular metal has suitable characteristics for use, and the seriousness whether the metal will be economically justifiable. The tests thus serve to eliminate a large number of expensive installations that might prove unsuitable in service. Following a preliminary choice a test installation will determine whether extensive replacement is justified.

The unusually high figure indicated by Mr. Mackenzie for cast iron in 5 per cent hydrochloric acid was substantiated by data in other strengths of the same acid. With lower acid concentrations the cast iron showed a fairly rapid decrease in penetration. In practice, however, neither steel nor cast iron would be used for such a service but in test work they are included in the nature of standards for comparative purposes.

Mechanical work has definitely been shown to be detrimental to a metal under corrosive conditions; any treatment of this nature given by a manufacturer would naturally penalize such a test piece. Wherever information was available on finishing, that information has been included.

It is hoped that the data presented will enable readers to compare the service given by particular installations with the test results and to determine whether even better results may be expected by a suitable change of material, and also aid in the selection and limitation of test pieces when tests can be carried out under local conditions.

Materials Used in Oil-refinery Pumps

By A. E. HARNSEBERGER*

(New York Meeting, February, 1935)

It is obvious that details such as the physical and chemical properties and methods of heat-treating of the materials mentioned must be omitted in a paper on the subject of materials used in oil-refinery pumps¹. Only sufficient identification is given to enable the reader to find additional information from already published data. Also, the subject covers many operating conditions, but only the most important services can be discussed here.

To the oil refiner, the pumping equipment is of vital interest. Practically every refinery operation, from the charging of crude oil to a distillation unit to the shipping of refined products, involves some form of pumping machinery. Intermediate refining stages involve a great variety of pumping machinery to carry out successfully the aims of the refinery technologist. Temperatures at which oils are handled vary from -50°F. to 900°F. Pressure may vary from subatmospheric to 2000 lb. per sq. inch.

The selection of the proper materials involves a careful consideration of the conditions under which the particular pump must operate. The four most important considerations are temperature, pressure, corrosion, and abrasion or wear. Consideration of temperature may be divided into three parts: (1) extremely low temperatures of the order of -50°F. ; (2) temperatures at atmospheric or slightly above; (3) temperatures from 200° to 900°F. Pressures fall into two groups: (1) pressures reached by ordinary trade pumps of the order of 200 lb. per sq. in., (2) extreme pressure conditions involving pressures as high as 2000 lb. Noncorrosive and corrosive oils can be treated differently. Under the latter falls corrosion in the presence of water, which will occur up to 250°F. The second type of corrosion occurs in high-temperature pumping equipment, with temperatures from 450° to 900°F. , largely caused by sulfur compounds. There are also other corrosive conditions met with in refinery operations, particularly in the handling of acids, acid sludges and other specialized processes. These problems, although difficult to

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¹ A short list of materials mentioned will be found at the end of this paper.

cope with, are not major factors in refinery operations. Abrasion is a factor to contend with in handling certain hot oils containing coke or other impurities or in chemical processes in the handling of slurries made up of fuller's earth, copper oxide, etc. Wear occurs on parts in sliding contact.

The pump builders have made great progress in the past 10 years in providing the refiners with pumps built of materials that will successfully withstand operating conditions. Ten years ago the refiners had very little choice in the matter. They were forced to take standard pumps, mostly brass fitted, and worry along with them as best they could, frequently changing in their own shops to materials that would better withstand operating conditions. This situation is now changed, however, to the point where most of the builders are in a position to furnish the refiners with pumps built of materials that will allow operating conditions thought impossible a few years ago, and at the same time resist wear and corrosion to the point where their continued operation is practical. The chief consideration now is the economic factor of how much investment the refiner can afford for his equipment. This calls for close cooperation between the refinery engineer and the pump builder, in order that all known factors may be given consideration and the increment cost of the use of better materials determined before final purchase is decided upon. The frequency of replacement of worn or corroded parts on existing equipment operating under similar conditions of temperature, pressure and grade of oil furnishes a guide to the engineer as to the economic value of more expensive materials. Frequently, however, more expense is not involved but a wise choice of materials of nearly equal cost is called for. It is up to the refinery engineer to decide whether standby equipment will be used. In most cases it is more economical to install one high-grade piece of equipment and have one prime mover than to install a lower grade of equipment that will give trouble and necessitate standby equipment in order to insure continuity of operation of the particular process under consideration.

For convenience of discussion, the following survey is divided into: (A) general service pumps; (B) pumps used on distillation and cracking equipment handling oils up to 200° F.; (C) pumps used on distillation and cracking equipment handling oils up to 900° F.; (D) pumps used in refinery gas absorption plants; (E) pumps used to handle sludge acids; (F) pumps used on treating processes.

A. GENERAL SERVICE PUMPS

Into this group falls a wide variety of pumping equipment, including reciprocating, centrifugal and rotary pumps, handling a wide range of sweet as well as sour oils. Their use is confined largely to the transfer of oils from one process to another, delivery of oils to storage, and the

delivery of stored oils to loading racks or docks. Particularly pumps transferring sour straight run gasolines and naphthas from rundown tanks are frequently subject to deterioration because of moisture, alkalis, acids or dissolved sulfur compounds contained therein.

Reciprocating Pumps—Cold Service

The preference of the refiners is largely for equipment fitted with ferrous materials.

Fluid Ends.—Cast iron¹ up to 700 lb. is recommended. Cast² or forged³ steel is recommended for higher pressures.

Liners.—Cast iron mostly used, with some preference for Meehanite⁴ and Ni-Resist⁵; the latter being used where corrosive sour oils must be handled. Brass or bronze liners are not recommended.

Fluid Piston Packing.—Cast-iron rings give best results under average operating conditions. Multiple snap rings are preferred over the three-piece bull-ring construction.

Valves and Valve Seats.—Mechanical wear is probably more important in the selection of valves and seats than corrosion. Many of the pumps operate under poor suction conditions and are operated at excessive speeds in order to hasten transfers, causing valves to pound their seats. A light-weight stainless valve of the Durabla⁶ type will give good results. A composition valve such as a Bakelite impregnated canvass disk, or equivalent, working on a cast-iron or cast nickel-iron⁷ seat is also recommended. Cast iron or Ni-Resist wing-guided valves working on hardened steel seats show very satisfactory performance. Valves and seats made of aluminum give good service on sour oils where corrosion is more of a factor than wear. Many pumps are in use with bronze valves operating on bronze seats, but these will not wear as long as others mentioned above.

Fluid-end Piston Rods.—Wear is generally the chief consideration. Carburize-hardened S.A.E. 1020 and heat-treated S.A.E. 3140 or 6150 steels will give good service. If, however, the pumps are exposed to the weather and idle for considerable periods, these rods will rust and injure packing. In such cases a 13 per cent chromium-steel⁸ rod hardened to 300 Brinell, or a rod made from KA₂S⁹ should be used, and will justify the increased cost of the materials. Bronze rods are not recommended.

Centrifugal Pumps—Cold Service

Casings.—Cast iron is entirely satisfactory on this service up to 500 lb. From 500 to 1000 lb. a close-grained cast iron containing 1 per cent nickel is satisfactory. For higher pressures, cast or forged steel should be used.

Impellers.—Impellers made of cast iron are in general suitable for the conditions encountered in this type of service. Bronze impellers are a

little cheaper and if confined to use on noncorrosive oils will give satisfactory service. If extremely sour oils are being handled, such as the distillates from West Texas crude, Ni-Resist or 4 to 6 per cent chromium-steel¹⁰ impellers are recommended.

Casing Wearing Rings.—Cast-iron rings are usually satisfactory. Rings of hardened nickel iron will give longer service. If corrosion occurs on transfer pumps, Ni-Resist or 4 to 6 per cent chromium should be used.

Shaft Sleeves.—These are important parts of centrifugal pumps because corrosion or abrasion of the sleeves is certain to make the packing problem more difficult and leakage from stuffing boxes represents one of the refiner's most serious losses. Bronze and mild steel should be rejected as too soft to resist packing wear. Casehardened, cyanide-hardened or nitrided steel sleeves will give good service if there is little corrosion. Where corrosion is present, 4 to 6 per cent chromium hardened to 250 Brinell gives satisfactory service; 13 per cent chromium hardened to 300 Brinell, and KA₂S are used frequently with good results. Considerable depends upon the mechanical condition of the shaft, since if this does not run true vibration and excessive wear will result in spite of the materials used. Considerable judgment must also be exercised as to the type of packing and its application.

Rotary Pumps

Rotary pumps in this type of service are usually of ferrous construction.

Casings.—Cast iron is predominantly used.

Shafts and Rotors.—Hardened steel is necessary for long wear. Nitrided parts frequently are employed with good results. Hardened 4 to 6 per cent chromium or 13 per cent chromium steels should be used on corrosive services.

B. PUMPS USED ON DISTILLATION AND CRACKING EQUIPMENT HANDLING OILS UP TO 200° F.

Pumps in low-temperature service on these processes fall into three classes; charging pumps, product pumps and reflux pumps. The cold-charging pumps handling either crude oil or charging stock should utilize materials as mentioned in section A, whether direct acting, centrifugal, or rotary type of design. Product pumps used to remove from the system the heavier fractions such as gas-oil, wax distillate, or fuel oils, may be fitted in the same way as the cold-charging pumps. Reflux pumps generally present a difficult maintenance problem. The oil being handled is usually a light fraction taken from separators wherein sufficient time has

not been allowed for the settling out of moisture. Unless there is perfect neutralization in the oil streams, and this is rarely attained, small amounts of weak acid will be handled by the pumps, and this will cause a destructive corrosion of many of the working parts. Investigation on materials used on these pumps shows the following:

Reciprocating Reflux Pumps Handling Light Oil Fractions

Fluid Ends.—Cast iron generally used.

Liners.—Cast iron is largely used. Ni-Resist or hardened chromium-nickel iron¹¹ gives superior service. Ni-Resist will give better wear than indicated by its average hardness of 150 Brinell because it glazes in service.

Fluid Piston Packing.—Packings most generally used are either Rock-Hard, or equivalent, sectional Bakelite rings, or equivalent, and cast-iron rings, either of the three-piece bull-ring or the multiple snap-ring type. Where corrosion conditions are severe, the Bakelite sectional ring has the greatest promise when used on a hardened iron liner.

Valves and Valve Seats.—Bakelite disk valves, or equivalent, used in connection with brass, cast-iron, or nickel-iron seats with stainless or bronze valve stems show good service records. Light-weight Durabla type valves of stainless steel or Monel Metal used with brass, cast-iron, or nickel-iron seats give good service. Aluminum disk-type valves, because of their light weight and corrosion resistance, look promising after several tests. Wing-guided cast-iron or Ni-Resist valves with cast-iron or hardened steel seats give good service. Cast-brass or cast-iron disk-type valves are not recommended because of rapid wear and corrosion.

Fluid-end Piston Rods.—The rods on these pumps give the greatest amount of trouble. Ordinarily S.A.E. 1020 steel rods will give from one to three months service under average operating conditions. Porcelain-coated S.A.E. 1020 steel rods will give from three to six months service as an average. This process is still in the development stage. Chromium-plated rods in several instances have been successfully employed, but usually the plating fails within a short time. Worn rods built up with stainless steel by the metal spray process have shown from three to six months service. The ultimate possibilities of this method of resisting corrosion have not been fully studied. On one service test Inconel did not prove satisfactory. Fair results are being obtained on 13 per cent chromium steel either hardened to 300 Brinell before machining or machined and then heat-treated to 450 Brinell and ground to finish. Under the most severe conditions, KA₂S is recommended and will easily justify its increased cost. With this material, a useful service 10 times that of carbon steel is achieved.

Centrifugal Reflux Pumps Handling Light Oil Fractions

Casings.—Cast-iron casings show from one to five years service. When corrosion is severe, bronze has been used containing 75 per cent copper, 15 per cent lead, 10 per cent tin.

Impellers.—One to two years service may be expected from ferrous materials for this service. Because of corrosion of ferrous materials, various bronze compositions ranging from metal similar to Admiralty to a composition of 75 per cent copper, 15 per cent lead, 10 per cent tin alloy, are being used. Monel has been used successfully. Ni-Resist is reported to be better than bronze in several instances.

Casing Wearing Rings.—Many materials are being experimented with for this purpose. Bronze materials, of the compositions mentioned under the section on impellers, and Monel are being used. The successful use of nickel-molybdenum steel, carburized or casehardened, is reported. Also, various refiners are using nitrided steel, stellited steel, Ni-Resist, and 13 per cent chromium steel. Corrosion on pumps of this type is so complex that it is difficult to state which materials can be used most successfully without a service trial.

Stage Bushings.—Although the majority of centrifugal pumps used in reflux service are of single-stage design, occasionally multistage units are employed, of materials somewhat like the materials used for wearing rings mentioned above.

Shaft Sleeves.—The service life of shaft sleeves depends very much on such factors as packing wear, misalignment, shaft speed and corrosive elements in the oil. It follows that materials that may have the best corrosion resistance may not present the best wear resistance. Under conditions where corrosion is not severe, hardened carbon steel or nitrided steel sleeves will give satisfactory performance, but such material will not resist an appreciable amount of corrosion. A hard, acid-resisting bronze is sometimes used; it will resist corrosion but is subject to wear. Stellited sleeves show good corrosion and wear resistance but frequently fail because the coated surface cracks or chips off. Chromium plating has not been successful. Several experiments are being made with porcelain-coated sleeves, but the results are not available. If chipping of the surface can be prevented, this material should be ideal for the purpose. A 13 per cent chromium steel, hardened to 450 Brinell, gives fair service. Alloys of higher chromium content are of doubtful value because they cannot be heat-treated to a satisfactory hardness.

C. PUMPS USED ON DISTILLATION AND CRACKING EQUIPMENT HANDLING OILS UP TO 900° F.

In considering the subject of materials for refinery hot-oil pumps, several factors must be considered. Because of the presence of a varying

amount of sulfur compounds, the hot oils being handled may be corrosive if the temperature is greater than 450° F. This corrosion will be increased by turbulent flow conditions, which will prevail. In centrifugal pumps, because of high heads per stage, fairly high velocities may be expected, which presents an erosion factor. The strength of the fluid ends must be given consideration because of the high pressures and temperatures involved. Any materials that show the slightest tendency toward embrittlement should not be used in such parts. On the other hand, internal parts may be made of materials that might embrittle in service without hazard. Depending on the process, the hot oil will deposit more or less coke, which will build up in the fluid ends, suction eye of impellers, diffusers, and volutes and on the valves of reciprocating pumps, thereby affecting efficiency and capacity. Certain materials tend to accumulate coke less rapidly than others, particularly materials that resist corrosion to a greater degree. Another important factor to consider in the selection of materials is the abrasion of coke or foreign material being carried by the oil stream. The wear will increase rapidly the clearances of wearing rings of centrifugal pumps and cause rapid loss of efficiency unless resisted by the proper materials. In reciprocating pumps, rapid plunger, or liner and ring wear will result.

Reciprocating Hot-oil Pumps

Liquid Ends.—Cast iron, cast and forged carbon steel are used in this service. Cast iron, having a tensile strength of 30,000 lb., is used up to about 400° F. with a pressure limitation of about 500 lb. at this temperature. High-test cast iron^{1a}, or what is often called semisteel, having a tensile strength of 45,000 lb., may be used for a temperature of 450° F. and a pressure of 600 lb. For higher temperatures and pressures, steel castings, properly annealed, often are used and are recommended for temperatures up to 900° and 1000 lb. pressure. For the combination of the highest temperatures and highest pressures, the use of forged carbon steel is desirable not only from the standpoint of safety, but also because the cost is somewhat reduced because of the uniformity and dependability of the material. If the oil is particularly corrosive, the use of an alloy steel is recommended. Experience shows that chromium content in excess of 6 per cent is hardly necessary in these parts even under the most severe conditions. From experience on handling hot West Texas oils, 4 to 6 per cent chromium is recommended. One of the most important advantages of this alloy, even on noncorrosive service, is that it will accumulate coke deposit at a very much slower rate than plain carbon steel, thus reducing to a minimum the cost of cleaning.

Frequently, because of corrosion, refiners have inserted liners of 4 to 6 per cent chromium steel in the fluid passages of their reciprocating pumps,

particularly on the suction side, where corrosion seems to be much more likely than on the discharge side. Also, in steel castings, metal removed by corrosion has been replaced by building up the sections by welding with 4 to 6 per cent chromium or 18 per cent chromium, 8 per cent nickel-steel rod.

Liners.—A close-grained cast iron will give fair service where excessive abrasion or corrosion is not experienced. Meehanite metal, which can be hardened up to 500 Brinell, will give better service than cast iron. Ferrodur¹², having a hardness of 500 Brinell, has shown excellent results. This metal is somewhat brittle but not sufficiently brittle to make its use impractical. Ni-Resist, having a hardness of 150 Brinell, shows good results. The coefficient of expansion of Ni-Resist is somewhat higher than that of plain cast iron, and due allowance should be made therefor in high-temperature applications. For temperatures above 600° F. low-expansion highly alloyed nickel cast irons should be used in preference to the standard Ni-Resist. Centrifugally cast liners have been produced containing as high as 22 per cent chromium. It is extremely dense and close grained, having a normal Brinell hardness of 300, but can be heat-treated to 500 Brinell. This material, however, on account of the expense will find application only under the most severe corrosion and erosion.

Fluid Piston Packing.—These parts are generally of either the three-piece bull-ring construction or multi-snap-ring type. The latter is preferable. Cast-iron rings are most generally used. Better service, however, can be obtained from a hardened material such as chromium-nickel iron or Meehanite.

Piston Rods or Plungers.—Materials used for these parts should not be too brittle because of the shock they are subjected to. The corrosion problem is lessened somewhat compared to other pump parts, since when handling hot oils cooling of some sort is always applied to the stuffing boxes, usually in the form of water jackets, cooling of the interior of the plungers, or the injection of cold oil into the pump packing. Therefore, in considering materials for these parts, wear is usually of more consideration than corrosion. Regardless of materials, good judgment in the choice of packings is of prime importance. The following materials have all been successfully used under conditions where a moderately corrosive oil is being handled:

S.A.E. 1025 carburized and hardened to 450 Brinell.

Cast carbon steel having a hardness of 300 Brinell.

Chromium-nickel-molybdenum-vanadium steel having
a hardness of 350 to 400 Brinell.

Nitralloy with a nitriding period of 96 hours.

S.A.E. 6150 heat-treated to a hardness of 300 Brinell.

U.M.A. 5 having a hardness of 375 Brinell.

Low-carbon steel rods metallized with high-carbon steel.

In conditions where corrosion is experienced in spite of cooling the following materials have been successfully employed:

13 per cent chromium having a hardness of 300 Brinell.

KA₂S is not considered economical on account of its lack of hardness.

Chromium plating has a record of a few outstanding successes but many failures.

Valves and Valve Seats.—Cast iron for the low-pressure and temperature conditions and cast or forged carbon or alloy steel for higher temperatures and pressures are frequently used. If the oil, however, tends to deposit much carbon or is moderately corrosive, forged or cast 13 per cent chromium-steel valves should be used. A Brinell hardness of 300 for the valves and 350 for the seats is recommended.

Centrifugal Hot-oil Pumps

All materials used in hot-oil centrifugal pumps should have the same coefficient of expansion. For example, if KA₂S is used in combination with and closely fitted to other alloy steels having a much lower coefficient of expansion, it will result in the KA₂S parts becoming distorted, causing damage to the pump. This is particularly true of case wearing rings, impellers, impeller wearing rings and bushings.

Outer Casings.—Cast iron, cast steel and forged steel are used in this service. In general, the temperature and pressure limitations for these materials given under Reciprocating Hot-oil Pumps can be exceeded somewhat, since shock is eliminated. Good castings, properly annealed, will show a performance equal to forgings; however, they are difficult to secure. If the oil is particularly corrosive, the use of an alloy steel is recommended. A 4 to 6 per cent chromium alloy has proved very satisfactory.

Inner Casings.—Cast carbon steel, heat-treated, can be used. However, cast 4 to 6 per cent chromium alloy steel is preferable because it will resist corrosion and will accumulate coke at a much slower rate than plain carbon steel.

Case Stud Bolts.—In centrifugal hot-oil pumps, case stud bolts should receive particular attention because of the large joints involved. Under the most severe conditions the following composition is recommended: chromium, 5.0 to 6.0 per cent; tungsten, 0.75 to 1.25; carbon, 0.25 to 0.35; silicon, 0.5 max.; manganese, 0.5 max.; sulfur, 0.05 max.; phosphorus, 0.05 max. The final heat-treatment should be such as to produce the following minimum physical properties; tensile strength, 140,000 lb. per sq. in.; yield point, 126,000 lb. per sq. in.; elongation in 2 in., 17 per cent; reduction of area, 45 per cent; Brinell hardness, 270 to 300.

Impellers.—On noncorrosive oils, high-test cast iron and low-carbon steel impellers are being used successfully up to 900° F. Steel containing

13 per cent chromium is a widely used analysis under corrosive conditions; KA_2S and 25 per cent chromium, 12 per cent nickel are also used. Impellers made of these chromium steels show practically no corrosion or erosion after several years of service. It is a general practice to fit chromium-steel impellers with wearing rings faced with Stellite No. 1 on the wearing surface, which is heat-treated and carefully examined for surface cracks after treatment.

Casing Wearing Rings.—Frequently 13 per cent chromium alloy steel, forged and hardened to approximately 300 Brinell, is used. When corrosion is severe, KA_2S and 25 per cent chromium, 12 per cent nickel alloy are used.

Interstage Bushings.—A 4 to 6 per cent chromium steel, stellite, and a 13 per cent chromium steel hardened to 300 Brinell are used successfully for these parts. Where corrosion is not severe, low-carbon steel with a stellite surface is satisfactory.

Shaft Sleeves.—Where corrosion is not severe, stellite low-carbon steel shaft sleeves are satisfactory. Nitrided shaft sleeves show from four months to two years service. Chromium plating is reported as unsatisfactory. Stellite surface gives some trouble due to cracking but in general is the most satisfactory material. Usually it is applied to a 4 to 6 per cent chromium steel or to a 13 per cent chromium alloy steel. Under severe conditions of corrosion, 25 per cent chromium, 12 per cent nickel sleeves, not stellite, have given good service.

Balancing Disks and Breakdown Drums.—Stellite surfaces are largely used, being applied to bar-stock 4 to 6 per cent or 13 per cent chromium steels. Poldi¹³ is also used as a facing on these parts. It is extremely resistant to erosion and moderately so to corrosion. Application is expensive.

D. PUMPS USED IN GAS-ABSORPTION PLANTS

Pumps used in these processes are not subject to extremely high pressures or high temperatures. The maximum pressure is of the order of 300 lb. and the maximum temperature about 400° F. The materials used in these pumps are subject to the action of free sulfur, other sulfur compounds, the action of a solution of hydrogen sulfide and water and a certain amount of abrasion because of foreign particles, such as iron scale. Absorption-plant pumps handling lean oil can be fitted in somewhat the same manner as pumps under section A. If the oil is hot, section C should be referred to. Generally the temperature is not of much consequence, the resistance to wear being of primary consideration. The discussion below is intended to cover pumps handling the lighter fractions of absorption-plant operations, such as unstabilized gasoline and reflux materials, either to stills or stabilizers.

Reciprocating Absorption-plant Pumps Handling Light Fractions

Fluid Ends.—Cast iron and low-carbon steel are used. Close-grained cast iron containing 1 per cent nickel has been used on the higher pressures. Under severe corrosive conditions, Ni-Resist is recommended.

Liners.—Cast iron is the material most often used and is satisfactory for the majority of the conditions. Ni-Resist will more than double the service life of cast iron. Phosphor bronze has been used but there is no record of its service life compared with Ni-Resist.

Valves and Valve Seats.—Disk valves of the Bakelite type operating on cast-iron seats will give good service. Durable stainless valves on cast-iron seats are also very satisfactory. Cast-iron wing-guided valves with hardened steel seats give very good service. In time, however, cast iron collects foreign material and requires cleaning. Wing-guided valves of 4 to 6 per cent chromium steel or 13 per cent chromium will improve this condition and justify the extra expense.

Piston Packing.—Cast-iron rings are most generally used, but three-piece Bakelite rings operating on cast-iron liners will be more satisfactory. Rock-Hard, or equivalent, if properly installed, will also give good service in conjunction with cast-iron liners.

Piston Rods.—A 13 per cent chromium hardened to 300 Brinell or KA₂S rod is recommended. Nitrided Nitralloy rods have shown excessive pitting, and these particular rods were replaced by steel rods with a high-grade heavy chromium plating, which have given much longer life.

Centrifugal Absorption-plant Pumps Handling Light Fractions

Casings.—Same materials recommended as under Fluid Ends for Reciprocating Pumps.

Impellers.—Cast iron usually gives good service. If the oil is moderately corrosive, Ni-Resist should be used and may be fitted with 13 per cent chromium stellited wearing rings. After three years, 13 per cent chromium impellers show no corrosion. If conditions are not corrosive, a 75 per cent copper, 15 per cent lead, 10 per cent tin or 88 per cent copper, 10 per cent lead, 2 per cent tin, composition can be used. For good wear, however, they should be fitted with iron rings surfaced with No. 1 Stellite.

Casing Wearing Rings.—If conditions are not corrosive, either case-hardened steel or nickel-iron rings should be used. If corrosive, Ni-Resist or 13 per cent chromium alloy steel, heat-treated to 300 Brinell, should be used. The wearing surface of the chromium-alloy shaft sleeves can be stellited to improve service. In this service KA₂S is also satisfactory.

Shaft Sleeves.—Casehardened shaft sleeves will give good service if conditions are not corrosive. If conditions are corrosive, Ni-Resist or 11 to 13 per cent chromium alloy steel, heat-treated to 300 Brinell, should be used.

E. SLUDGE ACID PUMPS

Most refineries have the problem of disposing of sludge acid¹³ resulting from the treating of light and heavy oils with sulfuric acid. Sludge from light oil is of low viscosity and is easily handled at ordinary temperatures. Sludge from lubricating oils, on the other hand, is very viscous and contains considerable coke, and must be pumped at elevated temperatures, which increases the corrosion factor. The heavy sludges usually are handled at temperatures from 100° to 220° F. and at pressures varying from 25 to 150 lb. Since in most cases this sludge is blended with other fuels and burned in the refinery, the pumping equipment must be reliable. A Magma pump usually is used in transferring the heavy sludges from the agitators to the cooking kettles and in blending. Because at this point the sludge is not hot, these pumps do not give much trouble. After blending and heating, conventional-type reciprocating pumps, or sometimes rotary pumps, are used for supplying the burning system. Heating is sometimes carried out with open steam, which dilutes the acid and increases the corrosion possibilities. On the other hand, open steam tends to give a more uniform blend by keeping the mixture agitated. Definite recommendations in regard to acid pumps are very difficult to make in view of the fact that conditions of temperature, pressure, acid concentration and abrasion vary over a wide range. Usually the best combination of materials can be arrived at only after considerable experimentation.

Centrifugal Acid Pumps

These pumps are strictly limited to handling the sludges of lighter viscosity. Duriron¹⁴ is satisfactory if connections are arranged to avoid strains on the material, which fractures easily. Acid-resisting bronze gives fair service on all parts. Monel is equal or superior to bronze.

Reciprocating Acid Pumps

Fluid Ends.—Acid-resisting bronze or red brass is usually employed.

Liners.—Acid-resisting bronze or a bronze made to A.S.T.M. Specification B-60 or Monel Metal is used. Acid-resisting bronze of 85 per cent copper, 10 per cent tin, 5 per cent lead is recommended.

Piston and Piston Rings.—Meehanite, acid-resisting bronze and Monel are used.

Rods.—Tobin bronze or Monel may be used. Monel is reported to be superior.

Valves and Valve Seats.—Acid-resisting bronze or Monel is recommended.

Rotary Acid Pumps

These pumps usually have acid-resisting bronze cases and shafts and rotors either of acid-resisting bronze or of Monel. Sometimes the combination of acid-resisting bronze rotors and a Tempaloy¹⁵ shaft is incorporated. Other pumps have been built using hard lead cases with Illium rotors and shafts.

F. MISCELLANEOUS¹⁶ PROCESSES

Pumps Used in Continuous Treaters

Such pumps generally handle a mixture of concentrated sulfuric acid and oil or caustic soda of varying strengths and oil. In general the recommendations for general service pumps outlined in section A can be followed, except that Bakelite, bronze and aluminum valves should be avoided in the presence of caustic. Many other services in refinery operations require the application of special materials to pumping equipment, such as the handling of abrasive materials and the handling of various chemicals used in treating processes. Pump applications usually are of such a special nature that a general discussion is inadvisable.

AVAILABILITY OF MATERIALS

While much is still to be learned about the application of the various types of alloy steels to industrial uses, still it can be stated as a general proposition that rolled and forged products are obtainable for a wide variety of uses, that they are thoroughly reliable and their uses are justifiable on economic grounds. The alloy-steel foundry industry has been successful, through research and experience, in developing and working out the problems involved in supplying castings to meet the demands of the pump designer wherein no great sacrifice in pump efficiency has been necessary. Such research as has been conducted in the past 10 years in connection with alloy castings has stimulated efforts to produce better low-carbon castings. It can be said that the product of the average foundry today shows a marked improvement over the standard that formerly existed. In general, the high-chromium and high chromium-nickel steels involve casting difficulties. The relative castability and behavior of materials when pouring depends upon their composition, but this general statement must be qualified by the further statement that the design of the casting, the thickness of the metal sections, the uniformity of the adjoining sections, have an important influence on the foundryman's efforts to produce satisfactory and reliable castings. Although the 5 per cent chromium steels containing small percentages of molybdenum or tungsten are not usually classified with high-chromium and high chromium-nickel steels, particular mention must be made of them because of the useful service they perform as distinguished from

plain carbon steels in oil and steam service. The foundryman regards them as "tender." That is to say, they are hard to handle in the mold and have to be treated very respectfully in the cleaning and finishing shop. They have a greater tendency to crack in the mold than the 13 per cent chromium steels. The 5 per cent chromium alloy is air-hardening, and as such receives, as a rule, more extensive heat-treatments in the cleaning shop. The 13 per cent chromium alloy is less tender than the 5 per cent chromium alloy, has a narrower range of fluidity, and must be more carefully watched to obviate porosity in the castings. This condition is particularly pronounced when the carbon content is low.

Nickel is the most common alloying element used in conjunction with chromium. The most common of the chromium-nickel alloys is the 18 per cent chromium, 8 per cent nickel composition, which has better castability than any of the straight chromium or other chromium-nickel alloy steels customarily used in pump manufacture. It has excellent fluidity, only slight tendency to crack in the molds, and good welding properties. As a matter of fact, it has even many foundry advantages over straight carbon steels, up to the point where cleaning operations must be considered.

The behavior of chromium and chromium-nickel castings, as compared to carbon castings, is very noticeable in the cleaning room. Heads, gates and risers are readily removed from carbon castings with the oxyacetylene flame or cold saw. Alloy-steel castings in general are very difficult to handle by these methods. A localized heat produced by the electric arc, which actually melts off the gates and risers instead of burning them off, may often result in cracking the castings. As the section to be cut off increases in size, the problem becomes more serious. Preliminary heat-treatments varying with the composition are employed to obviate the danger of castings cracking during the removal of heads and gates or by welding operations in making repairs.

The limitations in size and composition of alloy for pump parts depend upon the design of the casting and the foundry equipment available.

The minimum size of impeller that is practical to cast depends on the design, relation of heavy and thin sections, type of alloy used, and the ratio of the width of water passage to the diameter of the impeller. It can be roughly said that the minimum thickness of metal section is approximately $\frac{1}{4}$ in. for impellers of 12-in. diameter; and $\frac{3}{8}$ in. for impellers of 20-in. diameter. The minimum practical width of oil passage is approximately $\frac{1}{4}$ in. for impellers up to 7 in. in diameter, and must be increased proportionately as the diameter of the impeller increases.

CONCLUSION

In reviewing the material requirements of refinery pumps, some definite needs for alloy-steel and iron parts are disclosed. The only thing

that restricts their use is their high initial cost. High cost does not necessarily represent excess profit but rather a lack of volume of any one alloy. Pump manufacturers should survey the entire chemical industry and determine whether the bulk of the conditions can be met by a few alloys, which could be produced in larger quantities at lower costs. As costs decrease a broader field of application will be found in the less corrosive services.

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MATERIALS MENTIONED

1. *Cast Iron*.—In this paper this term is intended to refer to a ferrous product, made either in a cupola, air furnace, or electric furnace, from a charge composed of pig iron and steel scrap. The total carbon, and ratio of combined carbon to uncombined carbon, and the silicon content, vary with thickness of sections to be cast and the service to which the parts are to be subjected.

1a.—Frequently cast-iron parts are said to be made of "high-strength iron," "high-test iron," or "semisteel." These products fall within the above definition of cast iron but usually contain a large percentage of steel scrap in furnace charge.

2. *Cast Steel*.—This term refers to a ferrous product made in an open-hearth or electric furnace from a charge of pig iron and steel scrap. It differs from cast iron in that the carbon is completely combined with the iron. A typical analysis, which would conform to A.S.T.M. Specification A-95-33, is as follows: C, 0.15 to 0.45 per cent; P, 0.05 max.; S, 0.06 max.; Si, not under 0.20; Mn, not under 0.50.

3. *Forged Steel*.—This term refers to a ferrous product made by the open-hearth or electric furnace. Sufficient discard is made from each ingot, before rolling into blooms, bars or slabs, to secure freedom from injurious piping and segregation. For certain high-grade forgings intended to be used under high pressure and temperature, the percentage of discard and reduction from ingot to bloom, bar, or slab are frequently specified. A typical analysis of carbon-steel forgings, which will conform to A.S.T.M. Specification A-18-30, grades B, C, D, E, F and G, is as follows: Mn, 0.40 to 0.80 per cent; P, 0.05 max.; S, 0.05 max. The carbon content is usually not specified but depends on the physical properties desired.

4. *Meehanite*.—A patent processed cast iron in which the graphitic carbon is dispersed through the iron very evenly in the form of small nodules, surrounded by a matrix of ferrite and pearlite. The analysis is approximately as follows: C, 2.40 to 2.70 per cent; Mn, 0.65 to 1.00; Si, 1.10 to 1.50; S, 0.05 to 0.14; P, 0.10 to 0.20.

5. *Ni-Resist*.—An alloy cast iron having a typical analysis as follows: Ni, 12.0 to 15.0 per cent; Cu, 5.0 to 7.0; Cr, 1.5 to 4.0; Mn, 1.0 to 1.5; Si, 1.25 to 2.0; C, 2.75 to 3.1; Fe, balance.

6. *Durabla Valve*.—A patented form of pump valve, differing from the usual form of disk valve only in the construction of the valve disk. The disk of the Durabla valve is made from a relatively light gage of die-formed sheet metal. In form it may be described as an annulus, flanged at the inner and outer diameter, the seating surfaces being adjacent to the two flanges. There is a single corrugation between the inner and outer seating surface. Its light weight eliminates pounding of the seats and reduces the inertia effect of the valve.

7. *Cast Nickel Iron*.—A cast iron with an alloying addition of nickel. A typical analysis is as follows: C, 3.25 per cent; Mn, 0.65; Si, 1.40; Ni, 0.75.

8. *13 Per Cent Chromium Steel*.—A typical analysis of the type of steel referred to in this paper is as follows: C, 0.30 to 0.40 per cent; Cr, 12.5 to 14.0; Mn, 0.30 to 0.50; Si, 0.50 maximum.

Heat treatment for Brinell hardness 450 to 500: Heat to 1750° F., quench in oil, draw at 390° F.

Heat treatment for Brinell hardness of 300: Heat to 1750° F., quench in oil, draw at 1050° F.

It is necessary to completely clean this type of steel after heat-treatment, in order to obtain the best corrosion resistance. It is recommended that the steel always be ground, or otherwise highly polished.

9. *KA₂S*.—A stainless steel of the following composition: C, 0.07 per cent max.; Cr, 16.50 to 20.0; Ni, 7.00 to 10.5; Mn, 0.60 max.; P, 0.03 max.; S, 0.03 max.; Si, 0.75 max.

10. *4 to 6 Per Cent Chromium*.—A typical analysis is as follows: C, 0.21 to 0.30 per cent; Cr, 4.5 to 6.5; Mo, 0.40 to 0.65; Si, 0.30 to 0.50; P, 0.05 max.; Mn, 0.45 to 0.75; S, 0.05 max. For best corrosion resistance, the following heat-treatment is recommended:

Cast 4 to 6 Per Cent Chromium: (1) Normalize at 1750° to 1800° F., (2) normalize at 1625° F., (3) draw at 1250° F. and furnace-cool to 700° F. (The soaking time for each heat-treating cycle should not be less than 5 hr., or ½ hr. for each ½ in. of metal section.)

Forged 4 to 6 Per Cent Chromium: After forging allow to cool in still air and reheat to 1650° to 1700° F., holding at heat 1½ hr. per inch of section and cool in still air to at least 1000° F. Reheat to 1350° to 1400° and furnace-cool after holding 1½ hr. per inch of section.

11. *Chromium-nickel Iron*.—A typical analysis of the type of cast chromium-nickel iron referred to in this paper is as follows: C, 3.00 per cent; Cr, 0.80; Ni, 2.75; Mn, 0.60; Si, 1.25.

Heat-treatment required for Brinell hardness of 300: Heat to 1550° to 1575° F.; quench in oil; draw at 800° to 1100° F., depending on section size.

12. *Ferrodur*.—This is the trade name of a centrifugally cast product made by the Janney Cylinder Co., Holmsburg, Pa. The exact analysis is not published. The author understands it to be a chromium-nickel iron.

13. *Poldi*.—This is the trade name of a steel made by the Poldi Hutt Stahl Werke, Austria. The complete analysis is not obtainable for publication.

14. *Duriron*.—This is the trade name of a cast iron made by the Duriron Company, Dayton, Ohio. The type analysis is as follows: Si, 14.5 per cent; Mn, 0.35; C, 0.85; Fe, balance.

15. *Tempaloy*.—The trade name adopted by the American Brass Co. for a nonferrous alloy having a type analysis as follows: Cu, 82.0 per cent; Fe, 2.5; Al, 9.5; Ni, 5.0; Mn, trace.

16. *Illium*.—The trade name of a nonferrous product made by the Burgess Parr Co., having a type analysis as follows: Ni, 60.0 per cent; Cr, 25.0; Cu, 8.0.

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